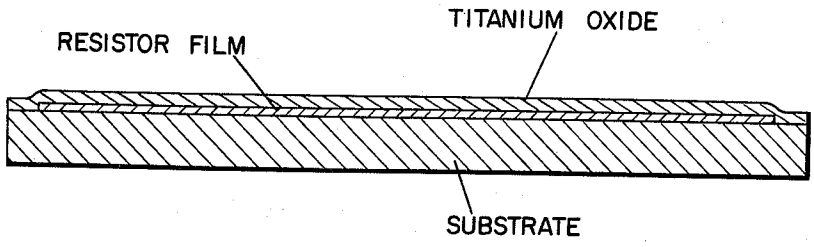
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PRECISION ELECTRICAL RESISTORS

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PRECISION ELECTRICAL RESISTORS

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This invention relates to precision electrical resistors and more particularly to a new method and new means for improving the characteristics of metal film resistors and protecting them against surface wear and degradation by the atmosphere.

In recent years considerable work has been done in connection with the problem of producing metal film resistance elements suitable for use in precision potentiometers. Considerable success has been achieved, particularly in connection with nickel chromium alloy films. Nickel chromium alloy films have gained substantial acceptance because they have (1) sufficiently high resistivities and (2) temperature coefficients of resistance which are satisfactory at moderate temperatures. However, nickel chromium alloy films have suffered from three major drawbacks. First of all, they are not particularly resistive to abrasion and tend to wear quite rapidly under the irritation of wiper contact. Secondly, they have a limited temperature range, being practically useless above a temperature range of 150° C. to 180° C. Thirdly, they have a moderately high positive temperature coefficient, generally approximating fifty to one hundred parts per million per degree centigrade. These limitations of nickel chromium alloy films heretofore produced has prevented obtainment of a suitable metal film potentiometer capable of operation at temperatures between −55° C. and +250° C. Other metal alloy film resistance elements have suffered from comparable or the same drawbacks.

Accordingly, the primary object of the present invention is to provide a method and means for improving the characteristics of metal film resistors and protecting them against degradation by the atmosphere.

A more specific object of the present invention is to provide a method and means for improving the characteristics of nickel chromium alloy film resistors so that they will resist abrasion, withstand high temperatures, and have a relatively low temperature coefficient of resistance.

Other objects and many of the attendant advantages of the present invention are apparent from the following detailed specification when considered together with the accompanying drawing which is an enlarged cross-section of a resistor embodying the invention.

Essentially, the present invention is based on the concept of applying a protective titanium layer over a metal film resistor so as to increase to an appreciable degree the film's resistance to abrasion and also to improve the ability of the film to withstand high temperatures.

The present invention contemplates the application of a protective layer of titanium oxide over the entire surface area of the metal film resistor so as to fully protect it from the atmosphere. The titanium oxide is applied as pure titanium metal, the metal being vacuum deposited upon the resistive metal film. After deposition of the titanium metal, the coated film is removed from vacuum and heated in an air or oxygen atmosphere for a suitable period of time at an elevated temperature, preferably about ten hours at about 425° C. This heating step causes conversion of the titanium metal to titanium oxide. The composition of the oxide formed is between $TiO_{1.6}$ and $TiO_{1.9}$. Although this oxide is non-stoichiometric, it has the rutile form of the stoichiometric TiO_2. Since the exact relationship between titanium and oxygen is unknown, it will be referred to as TiO_x.

A cross-section of a resistor embodying the invention

is shown in the accompanying drawing. The resistor comprises a supporting substrate of insulating material having on one surface thereof a resistive film of suitable composition. Overlying the resistive film is a protective layer of titanium oxide deposited and treated in accordance with the present invention.

The type of vacuum deposition apparatus employed in the practice of the present invention is not critical and various forms already well known in the art may be employed without any departure from the steps or principles herein disclosed. A preferred form of vacuum deposition apparatus and the one utilized in the examples hereinafter set forth is illustrated and described in a copending application of William J. MacDonald for Rhodium Germanium Film Resistor, Serial No. 759,165, filed September 5, 1958, now U.S. Patent No. 3,015,587, issued January 2, 1962. Described briefly, said preferred apparatus comprises a vacuum chamber in which is mounted a rotatable holder for a substrate on which a resistive film is to be deposited. The holder is rotated at a uniform speed by an electric motor. Directly in front of and about six inches away from the holder is a helical tungsten filament which is mounted so that an electric current can be passed through it. On this filament is secured the metals which are to be deposited as a resistive film or the titanium which is to be deposited as a protective coat for the resistive film. The metals are secured to the filament by electrolytic deposition or by fusion under a reducing, e.g. hydrogen, atmosphere. The filament is heated by an electric current to a temperature above the melting points of the metals, causing them to evaporate. The atoms of the evaporated metals impinge on the substrate in the holder and deposit thereon as a thin uniform film. The electric current is discontinued after all of the metals have evaporated from the helix. To facilitate deposition the substrate is preheated to a suitable temperature, e.g. 150° C. to 350° C., by means of one or more small filament heaters located proximate to the substrate holder. With this preferred apparatus air can be evacuated to a pressure level of between approximately 5×10^{-4} and 1×10^{-6} mm. Hg prior to evaporation of the metals from the tungsten helix.

Following are several examples of the manner in which the present invention is carried out with the foregoing apparatus. The first example is the preferred form of the invention.

Example I

Nickel and chromium are fused onto the tungsten helix in approximately 58 to 42 proportions by weight, with the total amount of nickel and chromium being sufficient to produce a deposited film having a thickness of 200 angstroms. Into the substrate holder is placed a quartz substrate which has been polished, abraded, degreased, cleaned and dried in accordance with procedures well known to persons skilled in the art. Then the substrate is preheated to a temperature of approximately 350° C. and while this occurs the chamber is evacuated. Thereafter, an electric current is passed through the tungsten helix to heat it to a temperature sufficient to evaporate the nickel and chromium from the helix. The evaporated metals are deposited on the quartz in a thin homogeneous film comprising approximately 80% nickel and 20% chromium. It is to be noted that some chromium is lost during the evaporation process. How or why this occurs is not clear. However, to offset this loss, the proportion of chromium applied to the helix is made higher than the proportion desired in the deposited film. On cooling this film has a temperature coefficient of resistance in the range of fifty to one hundred parts per million per degree centigrade. However, it is stable at temperatures only up to about 180° C. Above this temperature its resistance will change rapidly.

Onto a similar helix is fused titanium metal in an amount sufficient to produce a coating with a thickness of 400 angstrom units. After reheating of the substrate and re-evacuating of the chamber, this second helix is heated to a temperature sufficiently high to evaporate all of the titanium metal. The latter is deposited on the quartz substrate in fully covering relation with the previously formed nickel chromium film. This substrate is then removed from vacuum and is heated in air for approximately ten hours at 425° C. At the end of this time substantially all of the titanium metal will have been converted to the rutile form, TiO_x.

After this ten hour heating period, the substrate is cooled to room temperature.

The resulting film resistor is greatly superior to the film resistor without the titanium oxide coating. The layer of titanium oxide imparts three important characteristics to the base film.

First of all, since the titanium oxide is extremely hard, it increases the film's ability to withstand abrasion. As a consequence, the useful life of the unit is greatly increased. Moreover, less abrasion means less surface noise.

Secondly, the layer of titanium oxide improves the temperature stability of the film and increases its useful temperature range by isolating it from the effects of the atmosphere. It has been found that the majority of the resistance change of a properly prepared nickel chromium film resistor is due to surface oxidation. Placing the titanium oxide between the nickel chromium film and the atmosphere greatly reduces the rate of change of the resistive film. Under these conditions the only oxygen which reaches the nickel chromium film is that oxygen which diffuses through the protective layer. The diffusion rate of oxygen through the titanium oxide is such that the rate of change of the nickel chromium film is reduced to approximately three to five percent in one thousand hours at 260° C.

Thirdly, in addition to increased resistance to abrasion and increased temperature stability, the positive temperature coefficient of resistance of the nickel chromium film is reduced materially by the titanium oxide. Titanium has a relatively high negative temperature coefficient of resistance in a thin film form. Consequently, after the titanium has been applied over the nickel chromium film, but prior to its conversion to titanium oxide, the overall temperature coefficient of resistance of the sandwich, i.e., the resistive film plus the titanium protective overcoat, is negative. However, when the sandwich is heated to convert the titanium to titanium oxide, the temperature coefficient of resistance goes back to zero and rises again on the plus side. The finished product in this example will have a temperature coefficient of resistance of about 0–50 parts per million per degree centigrade. By varying the thickness of titanium and the length of the oxidizing period, the temperature coefficient of resistance can thus be controlled.

Thus, as a consequence of the present invention, it is possible to provide nickel chromium films which have a very low temperature coefficient of resistance, high temperature stability, and high resistance to abrasion. Resistance films produced according to this example are quite suitable for use in potentiometers to be used at temperatures between −55° C. and +250° C.

Example II

The tungsten helix is coated with a mixture of nickel, chromium, and rhodium in amounts sufficient to produce a deposited film resistance measuring 250 angstrom units thick, the mixture comprising four parts nickel, one part chromium, and two parts rhodium. A borosilicate glass substrate is inserted in the apparatus and an electric current is passed through the helix to evaporate the metals coated thereon. The metals are evaporated and deposited as a film on the substrate according to the same procedure as in Example I. Thereafter, a titanium coating measuring 300 angstrom units thick is deposited over the film resistor in the same manner as in Example I. Then the borosilicate glass substrate is heated in air at a temperature of approximately 425° C. for a period of approximately eleven hours. At the end of this time, substantially all of the titanium metal will be converted to titanium oxide TiO_x. As with the product of Example I, the resulting film resistor has an excellent resistance to abrasion and has improved stability against temperature changes. Its temperature coefficient of resistance has a value of 0–25 parts per million per degree centigrade.

Obviously, the specific temperatures given hereinabove may be varied without departing from the principles of the present invention. Thus, for example, the curing of the titanium film can be accomplished at temperatures ranging from approximately 390° C. to 500° C. with corresponding longer and shorter heating periods. Preferably, however, the curing should be executed at a temperature of approximately 400–425° C. Within this temperature range the time of curing is reasonable and consistent results are obtainable.

It is to be observed that the thickness of the titanium oxide coating may be varied. In practice it is preferred that the thickness be about 300–400 angstrom units since this range provides a good balance of temperature stability and contact resistance. Greater thickness will provide better temperature stability but will also provide excessive contact resistances.

In this connection it is to be observed that titanium dioxide (TiO_2) is an insulator. However, this invention causes the formation of a non-stoichiometric oxide of titanium with a composition in the range of $TiO_{1.6}$ to $TiO_{1.9}$. In this range of composition the oxide retains the rutile form of TiO_2 but is a "defect" structure. This defect structure causes the oxide to act as a semi-conductor. Furthermore, the oxide (TiO_x) is non-linear; that is, its conductance is much greater in one plane of the crystal than the other two planes.

The probability of crystals aligning themselves so as to allow conduction through the thin dimension of the film is very high, compared to the probability of alignment throughout the length of the film. The reason for this statement is obvious when it is realized that the thickness of the film often will be no greater than approximately 0.00003% of the length of the film.

It is in this way that this invention makes possible conduction through the protective oxide layer while the layer itself has little effect on the parameters of the original metal, e.g. nickel-chromium, film.

It is to be understood also that not only the composition but also the physical dimensions of the resistive film may be varied according to the electrical characteristics which are desired or needed, such variations being well within the scope of the present invention. Usually the metal film will have a thickness in the range of 100 to 1,000 angstrom units. However, greater thicknesses are also permissible.

It is to be observed that the present invention is not restricted to nickel chromium films but is applicable to other types of metal film resistors. In this connection is is to be understood that a metallic film resistor may be an alloy of two or more metals or simply a mixture of elements. Moreover, it may also include a minor amount of non-metals. Accordingly, as used herein the terms "metallic film" and "metal film resistor" include films which are wholly metallic or which include both metals and non-metals with the metal components present in a greater amount than the non-metal components. For the purposes of this invention the metal film resistors may include any of the following elements in various combinations with each other according to the particular resistance value and other characteristics which are desired: aluminum, antimony, barium, boron, cadmium, carbon, chromium, cobalt, copper, germanium, gold, indium, iridium,

iron, lead, magnesium, nickel, palladium, platinum, osmium, rhodium, ruthenium, silicon, silver, tin, vanadium, zinc, and zirconium. These films may be formed by evaporation deposition or by any other method or technique capable of producing a uniform film. Regardless of the combinations in which these elements are used or the manner in which the film is made, in each case the resulting resistive film will be covered with a titanium oxide coating applied in the manner previously described so as to protect against abrasion and stabilize against oxidation. However, the titanium oxide coating will effect an improvement in temperature coefficient of resistance only where the coefficient of the uncoated film is positive. Should the temperature coefficient of resistance of the uncoated film be negative, the titanium oxide overcoat cannot reduce such negative coefficients. However, by the use of proper oxidizing cycles, the other advantages of this invention can be achieved without degradation of this negative temperature coefficient.

Obviously, many other modifications and variations of the present invention are possible in the light of the foregoing teachings. It is to be understood, therefore, that the invention is not limited in its application to the details of composition and method specifically described hereinabove, and that within the scope of the appended claims, it may be practiced otherwise than as specifically described.

I claim:

1. A precision electrical resistor element comprising a rigid electrically non-conductive substrate, an electrically resistive metallic film deposited on said substrate, and a protective coating of titanium oxide fully overlying said film, said coating having a composition in the range of $TiO_{1.6}$ to $TiO_{1.9}$.

2. A precision electrical resistor as defined by claim 1 wherein said coating has a thickness in the range of 300–400 angstrom units.

3. A precision electrical resistor element as defined by claim 1 wherein said film has a positive temperature coefficient of resistance in the absence of said titanium oxide.

4. A precision electrical resistor element as defined by claim 1 and having a temperature coefficient of resistance in the range of 0–50 parts per million per degree centigrade.

5. A precision electrical resistor element as defined by claim 1 wherein said film comprises nickel and chromium.

6. A precision contact electrical resistor comprising a non-conductive substrate, an electrically resistive film deposited on said substrate, and a protective semi-conductive coating of non-stoichiometric titanium oxide fully overlying said film.

7. A precision electrical resistor element as defined by claim 6 wherein said protective coating has a thickness in the range of 300 to 400 angstrom units.

8. A precision electrical resistor comprising a nickel-chromium film coated with titanium oxide having a composition in the range of $TiO_{1.6}$ to $TiO_{1.9}$.

9. A precision electrical resistor comprising a nickel-chromium-rhodium film coated with titanium oxide having a composition in the range of $TiO_{1.6}$ to $TiO_{1.9}$.

10. A precision electrical resistor comprising a nickel-chromium film coated with titanium oxide, said titanium oxide having a thickness in the range of 300 to 400 angstrom units and being a semi-conductor of electricity.

11. The method of producing a precision electrical resistor comprising, providing a rigid substrate, depositing on said substrate a metallic electrically resistive film, thereafter depositing over said film a coating of titanium metal, and finally heating said substrate in an oxygen atmosphere at a temperature in the range of 390°–500° C. for a period of time sufficient to convert substantially all of said titanium metal to titanium oxide.

12. The method of claim 11 wherein said titanium metal coating has a thickness in the range of 300–400 angstrom units.

13. The method of claim 11 wherein said film normally has a positive temperature coefficient of resistance.

14. The method of claim 11 wherein said film comprises nickel and chromium.

15. The method of claim 11 wherein said film comprises nickel, chromium and rhodium.

16. The method of claim 11 wherein said titanium oxide coating is a semi-conductor of electricity.

17. A precision electrical resistor comprising a non-conductive substrate, an electrically resistive film deposited on said substrate, and a protective coating of electrically conductive titanium oxide fully overlying said film and having an exterior surface for engagement by a separate conductive contact member, said coating providing an electrical connection between said resistive film and an electrically conductive contact member brought into engagement with said surface.

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