

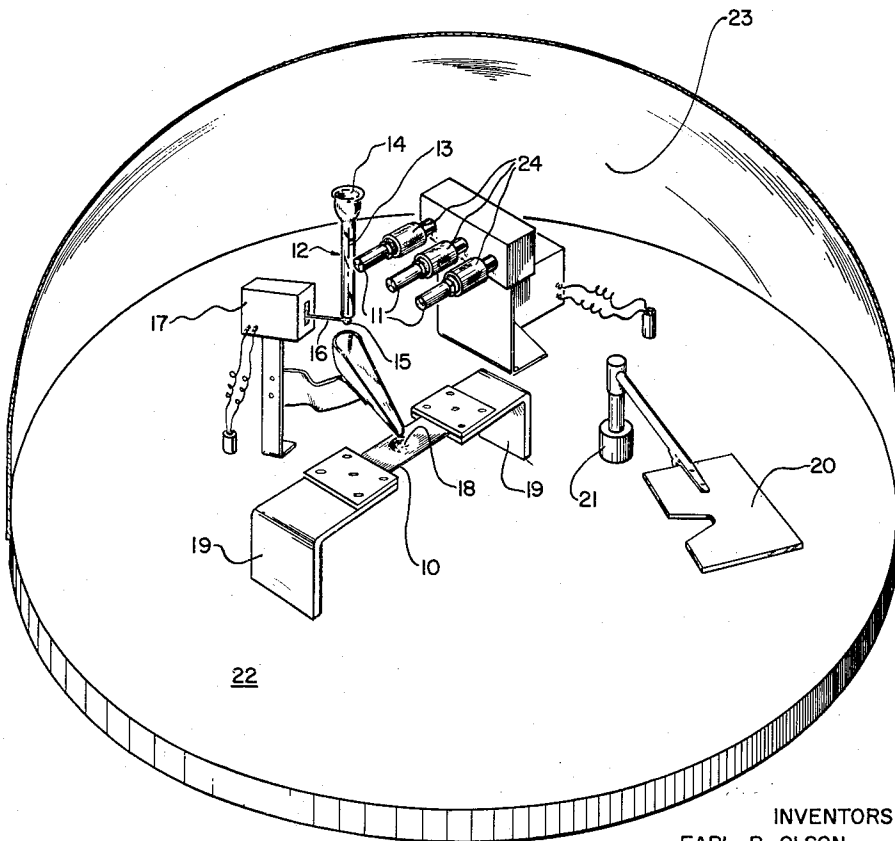
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FILM RESISTOR AND METHOD OF MAKING SAME

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FILM RESISTOR AND METHOD OF
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This invention relates to improved film resistors and methods of making them. More particularly, it relates to metallic film resistors having a low temperature coefficient of resistance, combined with a resistance which is high with respect to that of similar resistors having metallic films of equal thickness.

Generally, materials for film-type resistors have relatively low resistance per square. The resistance of a film can usually be increased by decreasing the film thickness. However, as the films are made thinner, they become more susceptible to oxidation and the effects of moisture and are usually very unstable. Also, such thin films often have high negative values of temperature coefficient of resistance. Films which are thicker and which may have a low temperature coefficient of resistance and good stability, have low resistances per square. Their properties can be duplicated or bettered by resistive materials in wire form.

It may be mentioned that mere knowledge of properties of materials in the bulk state has been found insufficient to enable accurate predictability of the properties of those materials when in the form of a thin film. Specifically, the properties mentioned below of an improved film resistor may be neither measured nor predicted accurately from properties of the bulk material.

It is an object of the present invention to provide a film resistor which combines the properties of low temperature coefficient of resistance, high resistance, good control of the value of the resistance, and high stability.

It is another object of this invention to provide a superior method for making the improved film resistor of the present invention.

Yet another object is to provide a superior resistive material in the form of a thin film.

Additional objects and features will become apparent as the description proceeds.

The film resistors of the present invention are prepared by evaporating a metallic bulk material in a high vacuum onto substrates of a ceramic material, such as polished vycor glass or glazed ceramic. Similar vacuum evaporation processes for the production of film resistors are well known. Of course, such variables as the temperature of evaporation, speed of rotation of the substrate, and degree of vacuum are determined by the properties desired, the nature of the material to be evaporated, and by the desired thickness of the film.

According to the present invention, a thin film of a homogeneous metal mixture of at least two metals is evaporated onto an insulating base material, the mixture including a substantial amount of at least one metal which is an easily-oxidizable metal whose oxide is highly resistive, and the mixture including a substantial amount of at least one conducting metal substantially more difficult to oxidize than the easily oxidizable metal. Then the deposited metal film is heat treated in an oxidizing atmosphere so as to selectively oxidize at least a substantial proportion of the easily oxidizable metal.

These steps greatly increase the resistance per square of the film by providing many areas of high resistivity in the film with tortuous conductive paths in the film. After the heat treatment step, to insure greater stability the film resistor may be protectively encapsulated to pre-

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vent further oxidation of the film. There is thus provided, in a metallic film resistor, a thin evaporated film comprising a metallic conducting matrix having nonconducting portions substantially evenly distributed therein.

It has been found that the combination of desirable properties mentioned above can best be attained by evaporating a homogeneous metal mixture of platinum and copper onto the film substrate. The highly preferred film can be produced from a binary alloy of platinum and copper, or from a mixture of powdered platinum and powdered copper. The resultant film is then heat treated at an elevated temperature in the presence of oxygen for a brief period of time. During heat treatment, the resistance of the film has been found to increase to about 100 times the initial low value. The composition of the film after heat treatment has been shown by electron diffraction measurements to be platinum-copper-copper oxide.

The above-mentioned properties are found in films produced from bulk materials ranging in composition by weight percent from 10 percent copper to 75 percent copper, the balance platinum. The composition of the film prior to heat treatment depends in part upon the method used for evaporating the bulk material. The film composition before heat treatment, with respect to the bulk material, will usually be slightly deficient in platinum. Even heat-treated films prepared from a platinum-copper alloy containing less than 10 percent by weight of copper have comparatively low resistance per square. When the copper content of the bulk material is greater than 75 percent by weight, the film produced therefrom is not sufficiently stable for usual resistor applications. Preferred film compositions range from about 15 percent to about 80 percent copper, by weight, the balance platinum.

Films with excellent properties were produced, for example, from bulk alloy compositions of platinum-25 percent copper and platinum-50 percent copper. Some spectrographic analyses of typical films produced from these alloys showed the metal content to be, respectively: platinum-30 percent copper and platinum-65 percent copper. This latter composition is highly preferred. Platinum-65 percent copper films may be used to obtain very high resistances, but are still stable and have a low temperature coefficient of resistance.

In the drawings:

FIG. 1 is a perspective view of the apparatus used to evaporate films of metals onto cylindrical substrates, illustrating a preferred method.

A preferred method for evaporating the platinum-copper films onto substrates in the present invention, illustrated by FIG. 1, is evaporation in a vacuum system of a powdered alloy from a hot container or boat, herein called a "powder-hot-boat" method. Such a method is described in the Journal of Applied Physics, vol. 19, pages 739-741 (August 1948). Several modifications to the method and of the device therein described were made. These modifications were necessary to permit the use of the high temperatures necessary to evaporate metals with a high melting point.

In the powder-hot-boat apparatus of the present invention a tungsten boat or holder 10 is resistance heated to about 2100 to 2300° C. Above the boat 10 are situated the substrates 11 on which the alloy is to be evaporated. When the boat 10 has reached temperature, a powder of the alloy to be evaporated is deposited into the hot boat 10 and the alloy is almost immediately evaporated onto the substrates 11.

In the present apparatus, the powder is deposited into the boat by a hopper 12. The hopper 12 is a capillary tube 13 flared at the entrance 14 to permit ease of loading. The discharge of the powder is controlled by a small

steel ball 15 pressed into the bottom of the capillary tube 13 and affixed to an extension 16 of the vibrating element of an ordinary door-bell buzzer 17. To assure a good seal at the outlet, the steel ball 15 is heated before being pressed into the end of the tube 13. The hopper 12 and steel-ball valve 15 were made virtually self-aligning by allowing the hopper 12 freedom of vertical motion with a slight degree of lateral play. The rate of powder feed, determined in part by the valve displacement, was most easily controlled by adding extra weights into the bowl of the hopper until the desired feed was obtained.

The boat 10 was of tungsten strip 2½ inches by ½-inch by ¼-inch thick with a large circular depression 18 in the center adapted to receive the powder. The boats can be purchased or readily made from tungsten strip. At boat temperatures of about 2300° C., the current through the boat 10 was about 300 amperes, necessitating the use of very heavy copper electrodes 19 (connected to a power supply) to hold the tungsten strip. The power supply used provided this current from a 5-volt, 400-ampere hookup.

A shutter 20 of aluminum was arranged so that it could be positioned between the boat 10 and the substrates 11 to be coated while the boat 10 was being brought to temperature. When the evaporation was about to begin, the shutter 20 was swung out of the way through a rotating seal 21 in the base plate 22 of the evaporation chamber 23.

In making the evaporation, the bell-jar vacuum system was pumped down to about 3×10^{-5} to 5×10^{-5} millimeters mercury. The substrates 11, supported usually at 10 centimeters above the boat 10, were being heated during this time. With the shutter 20 in place, the boat 10 was slowly brought to the desired temperature (determined by an optical pyrometer), the shutter 20 was removed, and the powder was sprinkled onto the hot boat 10 by activating the door-bell buzzer 17. A satisfactory rate of delivery of the powder was about 1 milligram per second. At the conclusion of the evaporation the shutter 20 was replaced. Air was admitted to the bell jar in which the evaporation was performed after a lapse of one-half hour, the period required for cooling of materials which became heated during evaporation.

A boat temperature of 2100° C. was suitable for platinum-base alloys. Very little loading of the boat with the alloy evaporated was observed in the powder-hot-boat method of evaporation.

Evaporation was made onto both cylindrical substrates, and flat substrates. In evaporating onto cylindrical substrates, as illustrated in FIG. 1, rotatable chucks 24 were supported over the powder-hot-boat 10. The chucks 24 were rotated in unison by a variable speed motor. The rate of drive used was about 1500 r.p.m., although the optimum speed of rotation was not determined. The substrates 11 were held in the chucks 24 and were heated prior to, and during, deposition of the alloy by radiation from a Nichrome heater.

Evaporation was also made onto polished flat Vycor ceramic substrates. The substrate heater element for the flat substrates was a thin molybdenum sheet sandwiched between Vycor plates, one end of the unit being clamped to a support arm. The flat substrates were held against one surface of the heater unit by an aluminum sleeve which gripped the extremities of the substrates.

The alloy to be evaporated was prepared by melting the constituents in an argon atmosphere by induction heating.

First a mixture of the constituent metals in powdered form was compressed into a pellet. Then the pellet was inserted into a crucible of spectrographically pure graphite for induction melting in argon. The alloy was retained in a molten state for about 30 seconds to improve homogeneity.

All alloys were powdered by filing. A magnet was passed through the filings to remove any iron that may

have been removed from the file. The filings were then sieved to a particle size of 100-mesh or less. The iron content after filing was measured and was extremely small and is believed to have had little effect on the properties of the films.

Clean substrates are essential to the production and reproduction of high-quality films. For the evaporations described herein, each substrate was scrubbed with a soft-bristled brush wet with a detergent solution. After a tap-water rinse, the substrates were allowed to soak for one-half hour in a hot saturated solution of CrO_3 to which a small amount of concentrated H_2SO_4 had been added. Most of the films were then immersed in concentrated HNO_3 for a few minutes, then in a strong solution of KOH for another few minutes. A very thorough rinse in running distilled water completed the cleaning operation until time to use the substrates for deposition of films. In some cases, the HNO_3 and KOH steps were omitted with no observable difference in cleanliness. The majority of the substrates were kept in distilled water until needed. Immediately prior to use, the surface to be filmed was "flamed" with the tip of a gas-oxygen flame. The substrates were not unduly heated by this procedure. The ionized gases at the tip of the flame were thought to have a final cleaning effect on the surface of the substrates similar to that of the ionized gases present in the glow discharge method of final cleaning of films in an air atmosphere at reduced pressure. Some substrates were kept under methyl alcohol rather than distilled water after cleaning. The substrates appeared equally clean, irrespective of the storage solution. The final immersion in alcohol appeared to shorten the pump-down time of the vacuum system, alcohol having a higher vapor pressure than water.

The preferred heat treatment for the platinum-copper films of the present invention consists of heating to a temperature of from about 150° C. for at least about one hour to about 350° C. for at least about one minute. The range of possible useful film thickness is from about 50 angstroms to about 1500 angstroms. The heat treatment, of course, is conducted in the presence of oxygen.

As an indication of the high stability and low temperature coefficient of resistance (TC) of these films, the following table is compiled from data gathered on typical heat-treated films of both Pt-25% Cu and Pt-50% Cu bulk alloy composition. As indicated, some of the films are on substrates of polished Vycor glass, others on glazed ceramic bases. All were on a load-life test for 1000 hours or longer. The load-life test consisted of maintaining the films in air at an ambient temperature of 100° C., some of the films being encapsulated in glass. A direct current was passed through the film to give an I²R loss of one watt per square inch of film surface.

Film Sample (Bulk Alloy Composition)	Base	Initial R/sq. (ohms/square)	Final R/sq. (ohms/square)	Percent Change in 1,000 hrs.	Average TC, p.p.m./° C.
Pt-50% Cu.....	Vycor Glass.....	1, 110	1, 125	+1.4	45
Pt-50% Cu.....	Glazed Ceramic.....	1, 280	1, 285	+0.4	79
Pt-50% Cu.....	Vycor Glass.....	1, 470	1, 493	+1.6	52
Pt-50% Cu.....	do.....	5, 900	6, 100	+3.4	64
Pt-50% Cu.....	do.....	5, 075	5, 300	+4.4	44
Pt-50% Cu.....	Glazed Ceramic.....	9, 600	9, 700	+1.0	19
Pt-50% Cu.....	do.....	13, 300	13, 280	-0.2	34
Pt-25% Cu.....	Vycor Glass.....	3, 300	3, 350	+1.5	-11
Pt-50% Cu.....	do.....	5, 550	5, 570	+0.4	62

¹ Encapsulated.

It is well known that the resistance of films on substrates of the proper geometry can be increased by spiraling. By this technique, the resistance of a film on the outer surface of a cylindrical substrate ¾ inch long by ¼ inch diameter, for example, can be increased as much as three thousandfold. Thus, such a film resistor of 5000 ohms resistance can be altered to one of as high as 15 megohms resistance.

The effect of temperature in producing a permanent resistance increase was examined for several of the platinum-copper (for example, platinum-25 percent copper) films. A recorder was used in conjunction with a constant current source to produce a continuous record of the deviation of resistance from the initial value as a function of temperature and time. In most cases where the film was placed in a preheated oven at 200° C., 250° C., or 300° C., resistance increased to a stable value within five minutes. The increase was nearly linear with time. The higher the temperature, the greater was the resistance change. That is, the resistance would become stable at a higher value of resistance. Where the film was placed in a cold oven and brought slowly to an elevated temperature, the resistance increase could be stopped at a predetermined value, as indicated by the recorder, by removal of the film from the oven. Encapsulation and hermetic sealing at a stage during the resistance increase effectively stops further oxidation of the copper, and a stable resistance is maintained at the predetermined level. At no time in working with this material was the temperature coefficient of resistance measured to be greater than 100 parts per million per degree centigrade.

The resistors of the present invention consistently provide films having resistances per square greater than 1000 ohms while the temperature coefficients of resistance are less than 100 parts per million per degree centigrade. There is thus provided, in a film-type resistor, a metallic film comprising at least 20 percent platinum, the film being from about 50 angstroms to about 1500 angstroms in thickness, which film has a resistance of at least 1000 ohms per square and yet a temperature coefficient of resistance less than 100 parts per million per degree centigrade.

Film resistors of other materials than copper and platinum were made and tested. The filament material for the evaporations described below was Tophet C, which consists of 61 percent nickel, 15 percent chromium, and the balance iron, as manufactured by the Wilbur B. Driver Company, of Newark, New Jersey.

The substrate material for the following described examples consisted of American lava-type ceramic designated Al Si Mag 196. The cylinders were one inch long with a $\frac{5}{16}$ -inch outer diameter and were glazed with a special glaze which matches the linear expansion (8.6×10^{-6} per ° C.) of the ceramic material. A $\frac{1}{8}$ -inch-wide electrode was fired onto each end of the cylinder, using a gold resinate manufactured by the Hanovia Chemical Works, of Newark, New Jersey. Immediately after this operation the substrates were ready for use without any further cleaning. The substrate surfaces appeared to be smooth and free from contamination. No substrate was heated before or during the evaporation process by an outside source at any of the evaporations described below.

For Tophet C, all the test examples showed an increase in resistance from the value measured immediately after evaporation of at least 100 percent after oxidation at 250° C. for 30 minutes. This increase, though small compared with the increase obtained with the platinum-copper system, could not be observed on films obtained under the same circumstances with Tophet A, an alloy with the same percentage proportions of nickel and chromium as Tophet C, but containing no iron. Films with Tophet A alloy change approximately 1 percent after being subjected to the identical condition described above for Tophet C. It thus appears that elective oxidation of the iron in Tophet C is at least partially responsible for the resistance increase.

It was suspected that a very irregular agglomeration of the chromium and nickel particles took place within these films, since the resistors showed a very high negative temperature coefficient of resistance.

Thus, although selective oxidation phenomena in film resistors may appear with several combinations of materials, the preferred combination of high resistance, stability, and low temperature coefficient of resistance is found to an unusual degree in the preferred copper-platinum system.

It will be understood, of course, that the various forms of the invention described herein are intended to be illustrative only and that various changes may be made by those skilled in the art in practicing the present invention.

What is claimed is:

1. A film-type resistor comprising a substrate having adherently fixed thereon a film consisting essentially of from about 15 percent to about 80 percent copper, by weight, the balance platinum, said film being from about 50 angstroms to about 1500 angstroms in thickness.

2. A film-type resistor comprising a substrate having adherently fixed thereon a film consisting essentially of about 65 percent copper, by weight, the balance platinum, said film being from about 50 angstroms to about 1500 angstroms in thickness.

3. A film-type resistor comprising a substrate having adherently fixed thereon a film consisting essentially of from about 15 percent to about 80 percent copper, by weight, the balance platinum, that has been heat-treated in an oxidizing atmosphere at a temperature of from about 150° C. for at least about one hour to about 350° C. for at least about one minute.

4. A film-type resistor comprising a substrate having adherently fixed thereon a metallic film consisting essentially of from about 15 percent to about 80 percent copper, by weight, the balance platinum, said film being from about 50 angstroms to about 1500 angstroms in thickness, and said film having a resistance of at least 1000 ohms per square.

5. In a film-type resistor, the film of claim 4, wherein said film has a temperature coefficient of resistance of less than 100 parts per million per degree centigrade.

6. A method of manufacturing film-type resistors which comprises: evaporating in vacuum at a temperature of at least 2000° C. a metallic charge onto an insulating base to form a metallic film on said base, said film having a thickness of from about 50 angstroms to about 1500 angstroms, and said metallic charge consisting essentially of from about 10 percent to about 75 percent copper, by weight, the balance platinum; and heat-treating said film in an oxidizing atmosphere at a temperature of from about 150° C. for at least about one hour to about 350° C. for at least about one minute.

7. A method of manufacturing film-type resistors which comprises: applying, in a thickness of from about 50 angstroms to about 1500 angstroms, a metallic film to an insulating base, said film consisting essentially of from about 15 percent to about 80 percent copper, by weight, the balance platinum; and heat-treating said film in an oxidizing atmosphere at a temperature of from about 150° C. for at least about one hour to about 350° C. for at least about one minute.

8. The method of claim 7 wherein the film which is applied consists essentially of about 65 percent copper, by weight, the balance platinum.

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