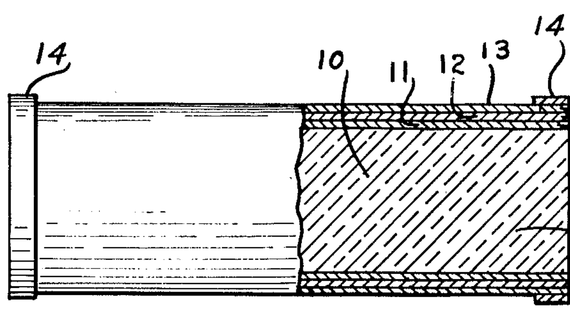
Nov. 9, 1965 E. M. GRIEST ETAL 3,217,281

ELECTRICAL RESISTOR

Filed May 28, 1962



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United States Patent Office

3,217,281

Patented Nov. 9, 1965

3,217,281
ELECTRICAL RESISTOR

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Filed May 28, 1962, Ser. No. 198,222
10 Claims. (Cl. 338—309)

This invention relates to improvements in electrical resistors of the type comprising a ceramic substrate, an electroconductive metal oxide film as a primary conducting element, and spaced terminals in electrical contact with the film conducting element.

Suitable materials and methods for producing such metal oxide films, and resistors incorporating such films as the conducting element thereof, are described in prior patents. Particular reference is made to United States Patents No. 2,564,706 and No. 2,564,707 issued in the name of John M. Mochel and No. 2,915,730 and No. 2,934,736 issued in the name of James K. Davis. In general, the method of film formation involves bringing a suitable material, or mixture of materials, in contact with a substrate at a temperature such that the contacting material thermally decomposes to deposit a thin adherent metal oxide film on the substrate. The resistivity characteristics of the film depend on the inherent resistivity of the film composition and on the film thickness. Mechanical expedients for increasing effective resistance, such as scribing to form a helical conducting path in the film, are also employed in resistor production.

Resistors embodying electroconductive metal oxide films provide distinct advantages over other types of resistors for many purposes and enjoy wide commercial application. For example, such films are now used in commercial resistors varying in size from one dissipating one-eighth watt in free air to a water-cooled type dissipating one hundred kilowatts. A particular advantage lies in the relative ease and economy of manufacture. Thus, the conducting metal oxide film may be continuously applied to glass cane as the cane is drawn from a reservoir of molten glass. The filmed cane is subsequently severed into suitable lengths that are provided with terminals and otherwise processed to provide completed resistor assemblies.

Electrical instability has been a particularly serious problem in the development of metal oxide film resistors. This condition of instability manifests itself by a gradual change in resistance during operation or service testing of a resistor. It has previously been recognized that both migrating alkali metal ions in the substrate material, and direct contact of the conducting film element with ambient atmosphere, can be major factors in electrical instability. In accordance with teachings in the previously mentioned Davis patents, it has become standard commercial practice to employ alkali-free substrate materials and to provide external protective coatings for electroconductive metal oxide resistors of the type under consideration.

These and other improvements have eliminated major causes of electrical instability and have greatly broadened the use of metal oxide film resistors. They have not, however, enabled such resistors to qualify as precision resistors. A precision film resistor is one meeting the requirements of Characteristic C in Military Specification MIL-R-10509C, Resistors, Fixed, Film (High Stability).

It has now been discovered that a ceramic material, even though it be free from migrating alkali metal ions, does not provide an entirely satisfactory substrate surface upon which to directly deposit the conducting metal oxide film element for a resistor. In particular, it has been found that improved stability is attained when a substantially non-conducting film composed of tin and antimony

oxides is deposited on a ceramic substrate surface prior to deposition of the conducting film element of a resistor. The non-conducting tin-antimony oxide film need only be of sufficient thickness to form a continuous film and hence, in effect, a substrate for the conducting film. The conducting element film and the non-conducting substrate film may contain the same oxide components, but with the components so proportioned as to have a much higher resistivity in the latter. The electrical stability of a resistor produced in this manner may be sufficiently improved to meet the conditions of the military specification earlier referred to, that is to provide a precision resistor as there defined.

It is recognized that interposition of an intermediate layer, including oxide films, between a conducting film and a glass substrate has previously been proposed. Thus, it is known to employ oxide films to promote adhesion of a metal film to a glass substrate. It is also known to employ such an intermediate film to minimize formation of haze, or light scattering, when a conducting oxide film is to be formed on a soda lime glass surface. However, the nature of the present improvement, and the phenomenon involved therein, are of a quite different nature.

As explained earlier, the problem of electrical instability in a film-type resistor, while alleviated considerably, nevertheless still persisted even when an essentially alkali-free glass or ceramic was employed as a film substrate. Characteristically, properly applied metal oxide films adhere tightly to glass and ceramic substrates. Further, various intermediate oxide films proposed as a means of minimizing haze formation and/or promoting metal adhesion may provide no benefit, or may even be detrimental, for present purposes. There is therefore no apparent relationship between the present improvement and prior proposals regarding barrier or adhesive films.

An improved resistor in accordance with the present invention comprises a ceramic substrate, an electroconductive metal oxide film as a primary conducting element, spaced terminal members in electrical contact with the primary conducting element, a second metal oxide film intermediate the primary conducting element and the ceramic substrate, the second metal oxide film being substantially non-conducting and composed essentially of tin and antimony oxides.

The ceramic substrate may be of any conventional form, such as tubular, rod or disc. Preferably, it is formed from an essentially alkali-free, alkaline earth aluminosilicate glass in accordance with the teachings of the earlier mentioned Davis patents. Alternatively, it may be a sintered ceramic, such as pure alumina, particularly where the substrate is of a disc shape readily produced from such a material. The term "ceramic" is here used in a generic sense to include glasses, glass-like materials, and conventional sintered ceramic materials.

The primary conducting element may be any of the conducting metal oxide films known to be useful for this purpose. A wide variety of such conducting films, and materials for their production, are disclosed in the patent literature. Tin oxide films containing up to a few percent antimony oxide, in accordance with the teachings of the earlier mentioned Mochel patents, have been found to be particularly effective for resistor production.

The intermediate substrate metal oxide film is substantially non-conducting with respect to the primary conducting element. In other words, it has a relatively low conductivity or, stated alternatively, a high resistivity. Its resistance value will normally be such that less than about one percent of the transverse current flow in a resistor assembly will occur in the substrate or intermediate film. In some instances, it may be permissible to have a slightly larger fraction, e.g. a few percent, of the total resistor current carried by the intermediate film.

This expedient can provide a balanced temperature coefficient where the primary conducting element has a positive temperature coefficient and is not otherwise balanced. However, it will ordinarily affect stability adversely, and may be utilized only where, and to the extent that, such adverse effect may be tolerated.

In any event, the essential purpose of the intermediate film is to provide an improved substrate surface upon which to deposit the conducting film. Thickness does not appear to be critical, but should be at least several hundred Angstrom units to insure a continuous film. On the other hand, it should be relatively thin in the interest of high resistivity and rapid deposition.

The substrate film is composed of tin and antimony oxides. Its constituent oxides may correspond to those of the primary conducting film, and the films may be produced by the same procedure of oxide deposition on a heated surface from a hydrolyzed and/or decomposable metal salt atmosphere. The proportion of antimony to tin is, however, much higher in the substrate film. For example, the latter will contain on the order of 30–60% antimony oxide, as calculated from the applied compounds, whereas the conducting film will usually contain about 1–3% antimony oxide. The higher antimony content films have standard resistance values of the order of fifty thousand ohms whereas the conducting films will be of the order of a hundred ohms or less. Actual values will depend on film thickness as well as on composition.

The exact manner in which improvement is afforded by the present invention is not fully understood. In accordance with one explanation, an abrupt change in molecular arrangement, or crystal structure pattern, at the interface between the conducting film and the substrate adversely affects electrical stability. The abrupt change in physical structure at this interface potentially introduces a stressed or otherwise unstable condition which may change during resistor service. This explanation reasons that the deposited film substrate provides a corresponding crystalline structure, whereas a glass substrate for example forces the initial atomic layers of an oxide film into a distorted unstable arrangement. It is further thought that the intermediate film provides a gradient structure between the primary conducting film and the ceramic substrate surface.

Several other possible explanations exist, in particular explanations based on a barrier layer to minimize chemical interaction or ion migration. However, the highly selective action of the intermediate layer, as hereafter shown, does not appear consistent with such explanations. In any event, the provision of an intermediate film in accordance with the invention has been shown to provide improvement in electrical stability by a factor of two or three over the optimum protected film structure heretofore available.

The single figure of the drawing illustrates a preferred embodiment of the invention and shows, partly in section, an electrical resistor composed of a cylindrical ceramic body provided with three superimposed metal oxide films and spaced terminal members.

In producing such a resistor and with reference to the drawings, a ceramic body **10**, e.g., a length of glass cane, is brought to a suitable film-forming temperature, e.g. about 650° C. The heated substrate **10** is then exposed to an atomized solution or vapors of a selected metal salt or salts, e.g. a mixture of tin and antimony chlorides, to produce an initial oxide layer or film **11**. Subsequent to formation of this initial film layer, and while the body is still maintained within the desired film-forming temperature range, primary conducting film **12** is formed over the substrate surface provided by film **11**. Thereafter, a further oxide film **13**, which may be of the same composition as film **11**, is deposited and terminal members **14** applied. As fully explained in the earlier Davis patents, the protective layer **13** will be so composed as to provide

transverse electrical contact between the terminals and the primary conducting film.

By way of further illustrating the invention, and more particularly the selectivity of the intermediate film with respect to improvement of electrical stability, the following specific comparative examples are presented:

EXAMPLE I

A group of three-layer film resistors was prepared by successive deposition of a low conductivity film, a conducting film, and a second low conductivity film on an essentially alkali-free alkaline earth aluminosilicate glass cane. Each film layer was deposited in the usual manner by contacting the cane, while heated to a coating temperature, with vapors from a suitably proportioned solution of the chlorides of tin and antimony. The films were deposited according to techniques well known in the art and fully set forth in the previously noted Mochel and Davis patents which describe procedures for deposting substantially homogeneous films of metal oxides by iridizing. The pertinent information regarding coating materials, thickness and film composition are as follows:

Solutions:

- Tin chloride (1.00 gm. $SnCl_4 \cdot 5H_2O$ in 1 ml. solution)
- Solvent—1 part conc. HCl, 5 parts H_2O
- Antimony chloride (1.00 gm. $SbCl_3$ in 1 ml. solution)
- Solvent—1 part conc. HCl, 1 part H_2O

Coating temperature ° C. 650
Cane diameter inches 0.141
Coating thickness (approx.):
- Under layer A. μ 850
- Conducting layer A. μ 600
- Cover layer A. μ 2,300

Solution Composition	Vol. percent $SnCl_4 \cdot 5H_2O$	Vol. percent $SbCl_3$	Resistance in ohms
Substrate film	40	60	125,000
Conducting film	97.75	2.25	500
Cover film	40	60	75,000

Four further groups of resistor elements were made up in identical fashion except that different coating materials were employed in deposting the substrate or glass-contacting film, thus providing different oxides in this film. For comparison, a further set of elements was made in which the substrate film was completely omitted, this set corresponding to commercial resistors produced in accordance with the Davis patent teachings.

Each set of coated glass cane elements was processed into NF 65 style, one-quarter watt, hermetically sealed resistors by application of terminal members on either end of the cane, followed by hermetic encapsulation of the coated cane in a glass envelope. The resistor units thus produced were placed on load test at full rated power at 125° C. ambient temperature. Resistance measurements were made on each resistor in each group both at the beginning and at the close of the load test period. The results are set forth in Table 1 below with "Max. ΔR" indicating the largest percentage change in resistance noted in each group and "Avg. ΔR" indicating the average change in resistance for all resistors in each group.

Table 1

DEPENDENCE OF LOAD STABILITY ON UNDERLAYER COMPOSITION

	Substrate Film Composition	Max. ΔR, percent	Avg. ΔR, percent	Time (hrs.)
1	None	+0.72	+0.57	1,000
2	SnO_2-Sb_2O_3	+0.26	+0.19	1,000
3	Fe_2O_3	−3.82	−1.51	1,000
4	NiO	−3.41	1.60	1,000
5	Al_2O_3	−7.12	−4.23	768

The results clearly show that the presence of a relatively non-conducting, tin-antimony oxide, substrate film provides an approximately three-fold improvement in electrical stability, whereas other substrate oxide films cause an even greater degree of instability than where no substrate film is employed.

EXAMPLE II

Two groups of resistors, corresponding to those identified in Table 1 as numbers 1 and 2 and prepared in identical manner, were subjected to a heat treatment at 550° C. for a period of ten minutes. This heat treatment was designed to simulate a typical firing schedule in which low resistivity terminal or contact members are fired on a filmed body to provide a resistor. The resistance of each resistor was measured before and after heat treatment and the average percentage change in resistance for each group of resistors was as follows:

Group	Type of Film	Resistance Change, percent
1	Duplex	+11.5
2	Triplex	+1.7

It will be noted that, under the conditions of this accentuated instability test, the presence of a substrate film provided a six-fold improvement in electrical stability.

While the invention has been described with respect to a specific preferred embodiment, it will be appreciated that the general principles are applicable to other types of conducting metal oxide film resistors as well. Accordingly, numerous variations and modifications of the invention will readily become apparent and are contemplated within the scope of the appended claims.

What is claimed is:

1. An electrical resistor comprising:
a first metal oxide film which is electroconductive and is the primary conducting element of the resistor,
a second metal oxide film of substantially homogeneous composition, on which said first metal oxide film is directly deposited and which
(1) consists essentially of antimony oxide and tin oxide, and
(2) has relatively low conductivity with respect to said first film,
a ceramic substrate which serves as a support for said second film, and
spaced terminal members in electrical contact with said first film.

2. A resistor in accordance with claim **1** wherein each of the metal oxide films is composed of tin and antimony oxides, the oxide proportions differing in the films.

3. A resistor in accordance with claim **1** additionally having a third metal oxide film of relatively low conductivity superimposed over the primary conducting film.

4. An electrical resistor comprising:
a first metal oxide film which is electroconductive and is the primary conducting element of the resistor,
a second metal oxide film of substantially homogeneous composition, on which said first metal oxide film is directly deposited and which
(1) consists essentially of from 30% to 60% antimony oxide and the balance tin oxide, and
(2) has relatively low conductivity with respect to said first film,
a ceramic substrate which serves as a support for said second film, and
spaced terminal members in electrical contact with said first film.

5. An electrical resistor comprising:
a first metal oxide film which is electroconductive and is the primary conducting element of the resistor and which consists essentially of tin oxide and antimony oxide,
a second metal oxide film of substantially homogeneous composition, on which said first metal oxide film is directly deposited and which
(1) consists essentially of from 30% to 60% antimony oxide and the balance tin oxide, and
(2) has relatively low conductivity with respect to said first film,
a ceramic substrate which serves as a support for said second film, and
spaced terminal members in electrical contact with said first film.

6. An electrical resistor comprising:
a first iridized metal oxide film which is the primary conducting element of the resistor and consists essentially of tin oxide and antimony oxide, and contains sufficient tin oxide so that said film is electroconductive,
a second iridized metal oxide film of substantially homogeneous composition, on which said first metal oxide film is directly deposited and which
(1) consists essentially of antimony oxide and tin oxide, and
(2) contains sufficient antimony oxide so that said film has relatively low conductivity with respect to said first film,
a ceramic substrate which serves as a support for said second film, and
spaced terminal members in electrical contact with said first film.

7. A resistor in accordance with claim **6** additionally having a third metal oxide film of relatively low conductivity superimposed over the primary conducting film.

8. In an electrical resistor comprising a ceramic substrate, an electroconductive metal oxide film as the primary conducting element and spaced terminal members in electrical contact with the primary conducting element,
the improvement consisting in a metal oxide film interposed between the ceramic substrate and said electroconductive metal oxide film so that the surfaces of said electroconductive metal oxide film and the interposed metal oxide film are in direct contact, the interposed metal oxide film being of relatively low conductivity with respect to said electroconductive film and being composed essentially of antimony oxide and tin oxide.

9. An electrical resistor comprising:
a first metal oxide film which is electroconductive and is the primary conducting element of the resistor,
a second metal oxide film, of substantially homogeneous composition, on which said first metal oxide film is directly deposited and which
(1) consists essentially of antimony oxide and tin oxide, and
(2) has relatively low conductivity with respect to said first film,
a ceramic support on which said second film is deposited, and
spaced terminal members in electrical contact with said first film.

10. An electrical resistor comprising:
a first metal oxide film which is electroconductive and is the primary conducting element of the resistor and which consists essentially of tin oxide and antimony oxide,
a second metal oxide film, of substantially homogeneous composition, on which said first metal oxide film is directly deposited and which
(1) consists essentially of antimony oxide and tin oxide, and
(2) has relatively low conductivity with respect to said first film,
a ceramic support on which said second film is deposited, and

spaced terminal members in electrical contact with said first film.

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