

[54] FILM RESISTOR AND METHOD

[75] Inventor: Ernel R. Winkler, Elmira, N.Y.

[73] Assignee: Corning Glass Works, Corning, N.Y.

[22] Filed: Dec. 16, 1974

[21] Appl. No.: 533,081

[52] U.S. Cl. 338/308; 29/610; 252/518;
427/101[51] Int. Cl.²..... H01C 1/02[58] Field of Search 29/620; 427/101; 338/308;
252/518

[56]

References Cited

UNITED STATES PATENTS

3,304,199	2/1967	Fabor, Sr.	252/518 X
3,766,511	10/1973	Vries.....	252/518 X

Primary Examiner—E. A. Goldberg

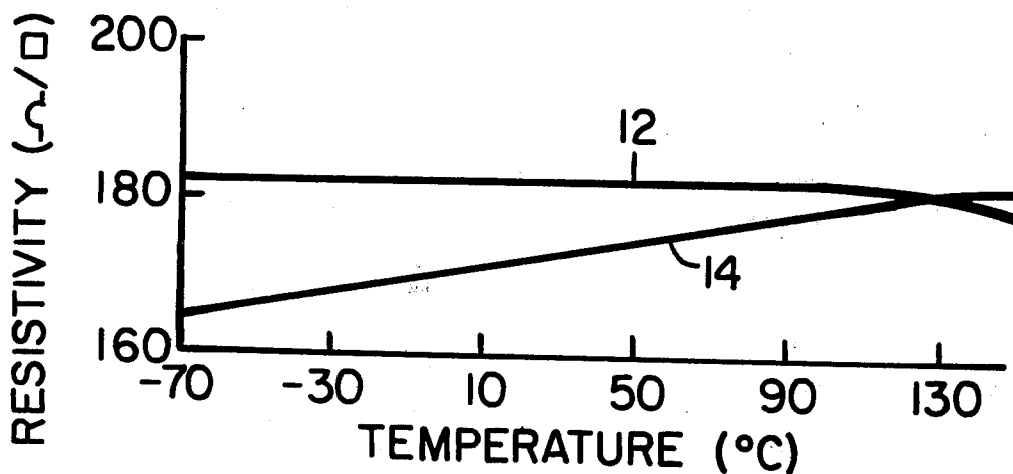
Attorney, Agent, or Firm—William J. Simmons, Jr.;
Walter S. Zebrowski; Clarence R. Patty, Jr.

[57]

ABSTRACT

Inexpensive resistor compositions which yield, upon firing, resistors having low TCR values. A temporary binder and finely divided particles of MoO_3 , a reducing agent and a glass containing PbO are mixed and the resultant paste is applied as a film to a substrate. The substrate and film are heated in an inert gas to a temperature sufficient to cause the PbO , MoO_3 and reducing agent to react to form PbMoO_4 and MoO_2 and to fuse the finely divided particles of glass. The resultant resistive film contains a continuous glassy phase having MoO_2 and PbMoO_4 particles uniformly dispersed throughout.

6 Claims, 5 Drawing Figures



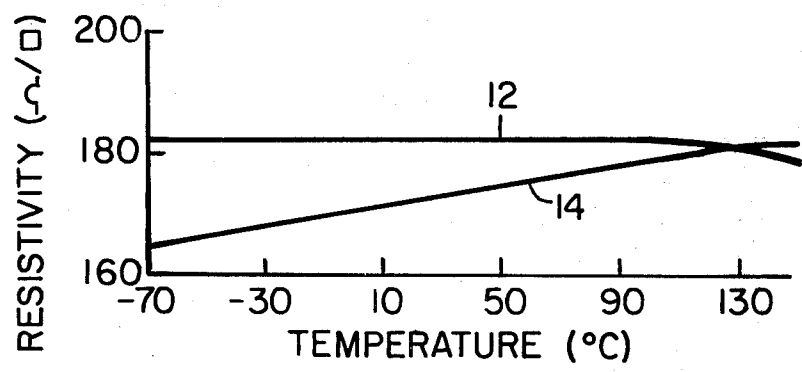


Fig. 1

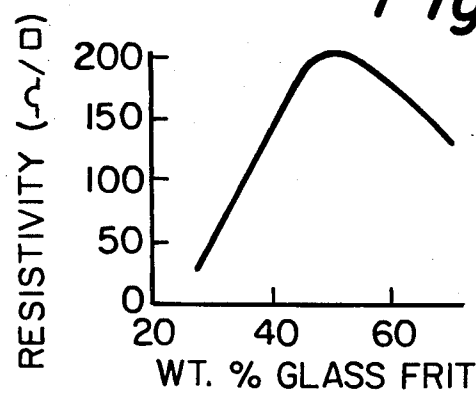


Fig. 2

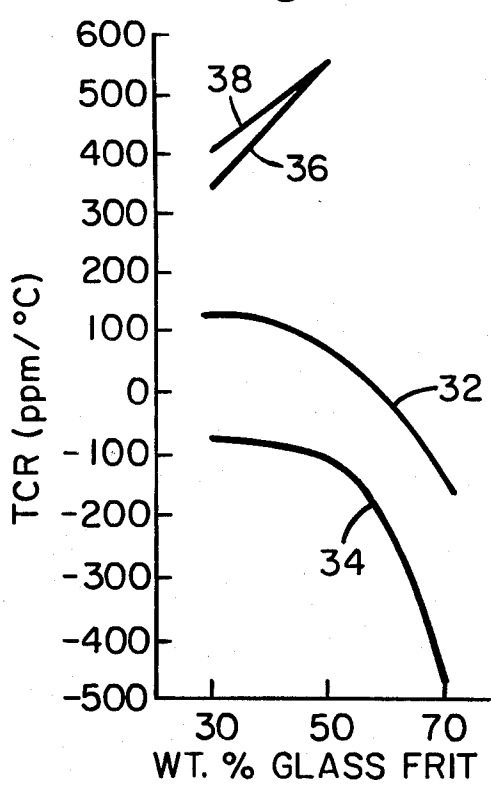
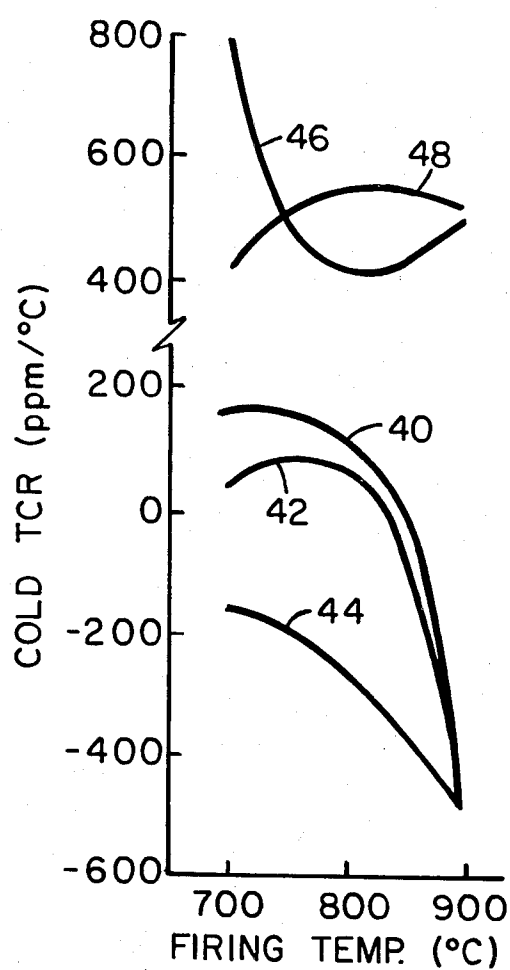
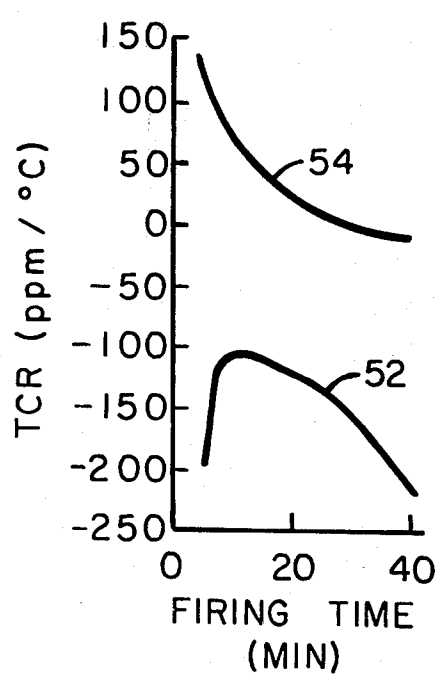


Fig. 3



FILM RESISTOR AND METHOD

BACKGROUND OF THE INVENTION

The present invention relates to electrical resistors and more particularly to oxide resistors and to a method for making the same.

Resistors are known which consist of a film of resistance material fused to a refractory, nonconductive base such as glass or ceramic. The resistive material may consist of a mixture of conductive and nonconductive materials and usually comprises a mixture of glass frit and finely divided particles of conductive material such as noble metal powders or conductive compounds thereof. A mixture of glass frit, conductive particles and a temporary binder is formed into a film of desired dimensions on the substrate by such methods as silk screening, brushing, dipping, spraying or the like. The characteristics of the resultant resistor may be modified by changing the ratio of glass frit to conductive particles and/or by combining this mixture with fillers or modifiers which are more or less conductive. The substrate and film are then fired at a temperature sufficient to fuse the particles of glass frit and produce a continuous glassy phase having conductive particles therein. The formation of such films is set forth in greater detail in "Thick Film Handbook", E. I. DuPont Company, (February 1970).

Until recently, the conductive portion of the paste employed to form these resistors has consisted of one or more precious metals and/or oxides thereof. The high cost of these precious metals and their oxides has encouraged a search for resistors wherein the conductive phase comprises a base metal. A resistor of this type is described in the publication "A High Quality, Base Metal, Thick Film Resistor System" by A. S. Laurie, Proceedings of the 1973 23rd Electronic Components Conference, pp. 137-139. The method disclosed in that publication involves the precipitation of a conductive oxide such as an oxide of molybdenum, tungsten, titanium or vanadium from a base glass. For example, a cadmium aluminoborate glass containing, as a dissolved component, molybdenum trioxide is melted, fritted and milled in a conventional manner. The resultant powdered glass is dispersed in a suitable temporary binder together with a small quantity of amorphous boron. The resultant paste is applied as a film to a substrate and then heated to fuse the glass particles and form a glassy film. Further heat treatment causes the boron to reduce the molybdenum trioxide to molybdenum dioxide which is precipitated as crystalline molybdenum dioxide which constitutes the conductive phase of the resultant resistor.

An attempt was made to form MoO₂-containing resistive films by the more conventional process of forming a paste comprising a conventional glass frit, powdered MoO₂ and a binder. The temperature coefficient of resistance (TCR) values of resistors formed from this paste ranged between 400 and 800 ppm/°C over a temperature range of -70°C to +150°C, depending upon firing parameters and percentage of glass frit in the paste. Resistors having such high values of TCR are commercially unacceptable for those applications where temperature stability is required.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a method of forming film resistors having low

values of TCR. Another object is to provide a method of forming film resistors comprising finely divided particles of MoO₂ dispersed throughout a glassy matrix.

Briefly, the method of this invention comprises forming a paste from a temporary binder and finely divided particles of MoO₃, an elemental reducing agent and a glass frit containing PbO in an amount effective for yielding PbMoO₄ upon reaction with the MoO₃ particles. A film of the paste is applied to a refractory non-conductive substrate. The substrate and paste film are heated in an inert gas to a temperature sufficient to cause a reaction between the PbO and the MoO₃ to form PbMoO₄ and between the MoO₃ and the reducing agent to form MoO₂ and an oxide of the reducing agent. The firing temperature must also be sufficiently high to fuse the finely divided particles of glass and thereby produce a continuous glassy phase having MoO₂ and PbMoO₄ particles uniformly dispersed throughout.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph of sheet resistivity v. temperature for reacted and unreacted resistive films.

FIG. 2 is a graph of sheet resistivity v. wt. percent glass in the film forming paste for reacted films.

FIG. 3 is a graph of TCR v. wt. percent glass frit in the film forming paste for both reacted and unreacted films.

FIG. 4 is a graph of cold TCR v. firing temperature for both reacted and unreacted films.

FIG. 5 is a graph of average TCR v. firing time for reacted films.

DETAILED DESCRIPTION

In view of the high TCR values exhibited by films consisting solely of MoO₂ particles dispersed in a glassy matrix, such films per se are not commercially acceptable for use in semiprecision film-type resistors. In the film resistor art two techniques have been used to tailor TCR to a low value. The first of these techniques involves the addition to the paste of another conducting phase in small quantity. For example, a semiconducting phase such as an oxide of the iron series may be added to adjust the TCR in a negative direction. The second technique involves a modification of the conductor itself by formation of a solid solution with other cations. In accordance with the present invention the first of these techniques is employed to provide MoO₂ resistors with low TCR values by forming the resistive film from a paste which results in the formation of a semiconductive phase as well as the conductive compound MoO₂. The essential constituents of the paste utilized to form this resistive film are MoO₃, a reducing agent, a lead oxide-containing glass frit and a suitable vehicle. The reducing agent is preferably one which will become a constituent of the resultant glassy film when oxidized during the firing of the paste film, the elements B, Si, Al, Ge, As, Sb or Bi being preferred. Thus, for example, the presence of MoO₃ and B in the paste results in the formation of MoO₂, which becomes the primary conducting phase of the resistor, and B₂O₃, which becomes a constituent of the glassy film. When the paste is formed from a lead oxide-containing glass frit, PbO from the glass and the MoO₃ react to form PbMoO₄. Resistors containing this semiconductive compound have exhibited much lower TCR values than those containing only MoO₂ particles dispersed in a glassy matrix. The glass frit must contain lead oxide in an amount

effective for yielding PbMoO_4 upon reaction with MoO_3 and preferably contains at least 35 wt. percent PbO . Moreover, for reasons hereinafter set forth, the fusing temperature of the glass frit should be below about 900°C . Although any of the well known lead glasses that fuse at temperatures below 900°C . may be employed, the preferred frit is a lead silicate glass. By "lead silicate" is meant any glass containing PbO and SiO_2 and optionally containing other glass forming oxides such as Al_2O_3 , ZnO , B_2O_3 and the like. Excluding the binder, film forming pastes conventionally contain between about 20 and 80 wt. percent glass frit. When the paste contains an insufficient amount of frit and fired films become rough, and when it contains too much frit, the fired film is electrically discontinuous. The preferred range for the method of this invention is 30–70 wt. percent glass frit in the paste.

The particle size of the glass frit, reducing agent and molybdenum trioxide particles should be less than 325 mesh and is preferably a few microns or less in size to provide reproducibility from one batch of resistive composition to the next. As used herein, the term "finely divided" indicates any particle size within this indicated range.

In the preparation of the film forming paste for use in preparing film type resistors by silk screening or other suitable techniques, any suitable temporary binder may be employed which, when combined with the particulate matter, forms a mixture having the desired viscosity characteristics. The binder must be capable of volatilizing during firing or be capable of being burned out during a prefiring heat treatment in air without forming residual phases that are detrimental to the resultant resistive film. Examples of suitable temporary binders are any one of the various organic liquids, with or without thickening and/or stabilizing agents. Examples of organic liquids that can be used are the higher alcohols; esters of such alcohols, e.g. the acetates and propionates; the terpenes such as pine oil, alpha- and beta-terpineol and the like; and solutions of resins such as the polymethacrylates of lower alcohols, or solutions of ethyl cellulose in a solvent. A binder comprising an organic polymer dissolved in an organic solvent has been found to provide the viscous printing qualities needed for machine printing.

After forming a paste from the binder and the finely divided particulate matter, a film is formed therefrom on a refractory, electrically nonconductive substrate of glass, ceramic or the like by any suitable technique such as silk screening, brushing or the like. The substrate and film are then fired in an inert atmosphere of nitrogen, argon, helium or the like at a temperature of at least 650°C to ensure that the paste constituents react to form MoO_2 and PbMoO_4 and to cause the glass frit to fuse and form a glassy film. Thus, the minimum firing temperature may be higher than 650°C , depending upon the fusing temperature of the glass frit. Because of the rapid increase in TCR at higher firing temperatures, the firing temperature should not exceed 900°C .

The following examples are illustrative of the method of preparing MoO_2 -containing resistive films in accordance with the present invention. Alumina substrates of 1 by 1.5 inch size and 0.036 inch thickness were employed in the formation of flat resistive films. The glass frit used in preparing the resistive compositions was a lead borosilicate glass having the following approximate composition: 63 wt. percent PbO , 25 wt. percent

B_2O_3 and 12 wt. percent SiO_2 . The glass batch was dry mixed, melted and thereafter milled to form a frit. The average particle size of the glass frit and the MoO_3 was in the $3\text{--}6\mu\text{m}$ range. The reducing agent was amorphous boron having a $5\mu\text{m}$ particle size. The temporary binder was prepared by dissolving ethyl cellulose in an organic solvent comprising a 1:2 mixture of iso-pentyl salicylate and 2-(2-butoxyethoxy) ethyl acetate.

A paste was prepared by mixing the glass frit, MoO_3 , B and the temporary binder. The required amount of binder was a function of the surface area of the inorganic constituents of the mixture as well as the final desired viscosity characteristic. Viscosity versus shear rate data were determined with a viscosimeter and additional amounts of the temporary binder were added to arrive at the desired viscosity. In some instances finely divided SiO_2 was added in small quantity to adjust viscosity.

A commercial printer was employed to print resistor patterns on the alumina substrates. The squeegee was made of polyurethane having a hardness of 70 Durometers and a width of 2.5 inches. Pressure on the squeegee was held at 2.5 lbs/inch with a speed of 6 inches/second. The resistor screen emulsion was 0.001 inch thick, with 200 mesh screen having 0.0021 inch openings. The coated substrates were fired in flowing N_2 in a tube-type furnace at 700° , 800° and 900°C . Since the MoO_2 particles in the resultant fired films are a product of a reaction between the MoO_3 and the reducing agent, boron, these resistors are hereinafter referred to as reacted resistors. Resistors were also formed by firing a film of paste containing only MoO_2 and a lead oxide-containing glass frit in addition to the temporary binder, which resistors are hereinafter referred to as unreacted resistors.

Reacted resistors containing 30, 50 and 70 wt. percent glass frit exhibited TCR values under ± 200 ppm/ $^\circ\text{C}$ with some being less than ± 100 ppm/ $^\circ\text{C}$. The overall temperature range for TCR measurement was -70° to $+150^\circ\text{C}$. TCR varied with glass content and with firing temperature and time. Reacted resistors exhibited much lower TCR values than did the unreacted resistors. A more detailed analysis of reacted resistors and a comparison thereof with unreacted resistors appears hereinbelow.

Sheet resistivity ρ_s for resistive films 0.15 in. $\times$ 0.15 in. is plotted in FIG. 1 as a function of temperature for both reacted and unreacted films, which are represented by curves 12 and 14, respectively. Both resistor types were made from pastes containing 50 wt. percent of the aforementioned lead borosilicate glass frit which contained 63 wt. percent PbO . Whereas curve 12 shows a near zero slope, curve 14 shows a metallic conductivity as indicated by a positive slope.

The effect of percentage of glass frit in the paste on sheet resistivity and TCR was determined by preparing pastes in which the glass frit comprised 30, 50 and 70 wt. percent of the inorganic particulate matter. It is noted that B_2O_3 resulting from the reaction of B and MoO_3 combines with the glass in the fired film, thereby resulting in an increase in the percentage of glass present in the reacted resistor film. Using average data of several samples, it was generally observed for both resistor types that sheet resistivity of films made from paste containing 50 wt. percent glass frit was higher than that for those made from paste containing 30 or 70 wt. percent glass frit. FIG. 2 is a graph of sheet resistivity ρ_s of reacted films plotted as a function of wt. per-

cent frit in the paste for resistors fired at 800°C for 9 minutes. It is expected that an increase in resistance would result from increasing the percentage of glass frit from 30 to 50 wt. percent since the ratio of the insulating glassy phase to the conductive phase increases. The mechanism for a decrease in resistance by increasing the percentage of glass frit from 50 to 70 wt. percent, which occurred quite generally in the case of reacted resistors, is not understood.

FIG. 3 illustrates the variation in TCR value for both reacted and unreacted resistors as a function of wt. percent glass frit in the paste. Curves 32 and 34 are the hot TCR and cold TCR curves for reacted films, respectively, and curves 36 and 38 are the hot TCR and cold TCR curves, respectively, for unreacted films. Curves 36 and 38 end at 50 wt. percent glass frit since unreacted films containing 70 wt. percent glass frit were often electrically discontinuous and insufficient TCR data were available for those films. The hot TCR curves were obtained for temperatures between 20° and 150°C, whereas the cold TCR curves were obtained for temperatures between -70° and 20°C. It was noted that the average film thickness of reacted films decreased from 12.7μm at 30 wt. percent glass frit to 6.1μm at 30

time at 800°C. Cold TCR for reacted films decreases almost exponentially from firing times of 5 to 40 minutes while hot TCR passes through a maximum at 10 minutes. Firing times between 7 and 12 minutes give the lowest overall TCR for reacted films. It was noted that sheet resistivity decreases almost exponentially as a function of firing time at 800°C for reacted films. Resistivity decreased from about 320 ohms per square for a 5 minute firing time to about 105 ohms per square for a firing time of 40 minutes.

A substantial difference was observed between reacted and unreacted resistors with respect to TCR. By choosing the proper firing conditions reacted resistive films could be formed having TCR values in the ±150 ppm/°C range whereas TCR values for unreacted resistors were over 400 ppm/°C. In order to ascertain the cause of the lower TCR values of reacted resistors, products of reactions occurring between various of the constituents of the film-forming paste were individually determined by X-ray diffraction (XRD). These constituents, their heat schedules and the XRD results are shown in Table II. For these tests the glass frit consisted of 63.1 wt. percent PbO, 24.2 wt. percent B₂O₃ and 14.5 wt. percent SiO₂.

TABLE II

Components of Reaction Non-glass (Mole Ratio)	wt.% Glass	Heat Schedule		XRD Phase Determination			
		T(°C)	t(min)	Major	Major	Minor	Trace
MoO ₃ B (3:2)	50	800	20	MoO ₂		PbMoO ₄	Glass
MoO ₂	50	800	20	MoO ₂		Glass	PbMoO ₄
MoO ₃ PbO (1:1)	0	700	30	PbMoO ₄			
MoO ₂ PbO (1:1)	0	700	30	PbMoO ₄	X*	MoO ₂	
MoO ₃	50	700	30	PbMoO ₄	MoO ₃	MoO ₂	

*Unidentified

wt. percent glass frit.

Table I indicates the effect of firing temperature on sheet resistivity for reacted films.

TABLE I

Wt. % Glass Frit	Resistivity in Ohms Per Square at Listed Firing Temperatures		
	700°C.	800°C.	900°C.
30	110ohms/□	50ohms/□	110ohms/□
50	305ohms/□	205ohms/□	315ohms/□
70	200ohms/□	135ohms/□	190ohms/□

The films were subjected to the temperatures indicated in Table I for 10 minutes.

FIG. 4 shows the variation of cold TCR with firing temperature for both reacted films and unreacted films, the films being held at firing temperature for 10 minutes. Curves 40, 42 and 44 are for reacted films made from 30, 50 and 70 wt. percent glass frit, respectively. Curves 46 and 48 are for unreacted films made from 30 and 50 wt. percent glass frit, respectively. FIG. 4 illustrates that reacted films exhibit much lower TCR values than unreacted films. The data for hot TCR values similarly illustrates the lower TCR values of reacted films. Both hot and cold TCR values for reacted films decrease very rapidly with firing temperatures above 800°C, and they are somewhat insensitive to firing temperature between 700° and 800°C. It is therefore preferred that the firing temperature does not exceed 900°C.

In FIG. 5 average hot and cold TCR are plotted in curves 52 and 54, respectively, as a function of firing

Relative peak intensities of the diffraction patterns determined the results listed in Table II. Several observations can be made from these results. The first reaction listed in the table is indicative of those reactions that resulted in the formation of resistive films. The particulate matter in the paste included 50 wt. percent glass frit, the remainder consisting essentially of MoO₃ and B which were present in the full mole ratio of 3:2. Firing the resultant paste at 800°C for 20 minutes resulted in a resistive film having a major amount of MoO₂ and a minor amount of PbMoO₄. It is estimated that the relative amounts of these two compounds present in the film are such that MoO₂ constitutes about 60-90 wt. percent of their total weight. In addition to the glass the reacted resistive films contained a major amount of MoO₂ and a minor amount of PbMoO₄ which was separately analyzed and determined to be a semiconductor. However, only a trace of PbMoO₄ formed with reaction of glass and MoO₂. MoO₃ and glass reacted more fully to form PbMoO₄ than did a mixture of MoO₃, B and glass. These results might be expected since Mo is in the +6 state in both MoO₃ and PbMoO₄, and with a mixture of B, MoO₃, and glass, the simultaneous reduction of MoO₃ to MoO₂ and reaction of MoO₃ with the host glass to form PbMoO₄ are competing for MoO₃. It is known that PbO and MoO₃ form PbMoO₄ at 460°C. In the formation of resistors, reaction is between MoO₃ and the lead oxide of the host glass, so the reaction temperature is likely higher. Since the unreacted resistors contained only a trace amount of PbMoO₄ whereas the reacted films contained a minor amount thereof, and since it would be expected that a semiconductive

material such as PbMoO_4 would adjust the film TCR value in a negative direction, the improvement in TCR exhibited by the reacted resistors of the present invention has been attributed to the presence of the PbMoO_4 .

XRD scans for a 2:3 molar mixture of B and MoO_3 were repeated at increasing temperatures to determine reaction products at those temperatures. Temperature was held for 30 min. at each level. The reaction was conducted under helium to prevent atmospheric oxidation. It was found that as temperature increased, the MoO_3 peak decreased while the peak for MoO_2 increased from zero intensity to a maximum at about 620°C where it remained. An intermediate product Mo_4O_{11} was observed, however. Its peak height increased to a maximum at about 570°C and then decreased to near zero as the MoO_2 peak reached a maximum and remained constant. A minor product believed to be Mo_2B was in question at higher temperatures. Thermal data of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were observed for the same B + MoO_3 mixture in nitrogen atmosphere. A double exothermic peak occurred with maximums at 570° and 620°C . These peaks correspond in temperature to the formation of Mo_4O_{11} for the lower temperature, lower intensity exotherm, and to the formation of MoO_2 for the higher temperature exotherm. A broad peak also occurs after heating, and it is at low 2θ diffraction angle. The only glass present is the B_2O_3 formed in the reaction. It is therefore preferred that reacted resistors be fired at a minimum temperature of about 700°C which is well beyond that required to react B and MoO_3 .

In summary, TCR is influenced by such variables as firing time and temperature, ratio of reducing agent to MoO_3 in the paste, percentage of glass frit in the paste and percentage of PbO in the frit. Unreacted resistors, which possessed only a trace amount of PbMoO_4 , have high values of TCR. The presence of the semiconductive compound PbMoO_4 in the resistive film lowers the TCR. If the method of the present invention were employed to form a resistive film and the TCR value of the resultant film were still too high, the process could be tailored to produce resistive films having lower TCR values. For example, a lower TCR value could be obtained by employing the same firing time and temperature and either increasing the percentage of glass frit in the paste or decreasing the percentage of reducing agent in the paste. Either of these changes in paste composition will favor the formation of PbMoO_4 and thus lower TCR. If the paste composition were main-

tained the same, TRC could be lowered by increasing the firing temperature.

I claim:

1. A method of making an electrical resistance element comprising the steps of

forming a paste containing a temporary binder and a mixture of inorganic particulate matter, said mixture including 30–70 wt. percent glass frit, the remainder consisting essentially of finely divided particles of MoO_3 and an elemental reducing agent, said glass frit containing lead oxide in an amount effective for yielding PbMoO_4 , the amount of said reducing agent in said mixture being sufficient to permit the formation of MoO_2 in an amount sufficient to form a continuous conductive path and of PbMoO_4 in an amount effective to modify the temperature coefficient of resistance of said conductive path,

applying a film of said paste to a refractory nonconductive substrate, and

heating said substrate and film in an inert atmosphere to a temperature of at least 650°C and which is sufficiently high to cause a reaction between the PbO in the glass frit and the MoO_3 to form PbMoO_4 and between MoO_3 and said reducing agent to form MoO_2 and an oxide of said reducing agent, said temperature also being sufficiently high to fuse said finely divided particles of glass frit and produce a continuous glassy phase having particles of MoO_2 and PbMoO_4 uniformly dispersed throughout.

2. A method in accordance with claim 1 wherein the step of heating comprises subjecting said substrate and film to a temperature between 700° and 900°C .

3. A method in accordance with claim 2 wherein said step of heating is continued for a period of time between 7 and 12 minutes.

4. A method in accordance with claim 3 wherein said glass frit contains at least 35 wt. percent PbO .

5. A method in accordance with claim 4 wherein said reducing agent is selected from the group consisting of B, Si, Al, Ge, As, Sb, and Bi.

6. An electrical resistor of the type comprising a substantially nonconductive substrate having a conductive film on the surface thereof, said conductive film being characterized in that it comprises finely divided particles of MoO_2 and PbMoO_4 uniformly dispersed in an electrically nonconductive fused glass matrix, said MoO_2 constituting the conductive phase of said film and said PbMoO_4 being present in an amount effective to lower the temperature coefficient of resistance of said film.

* * * * *