

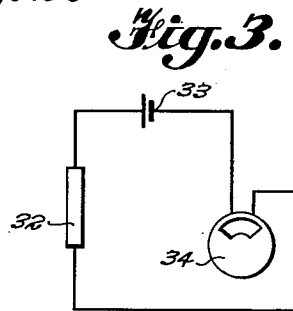
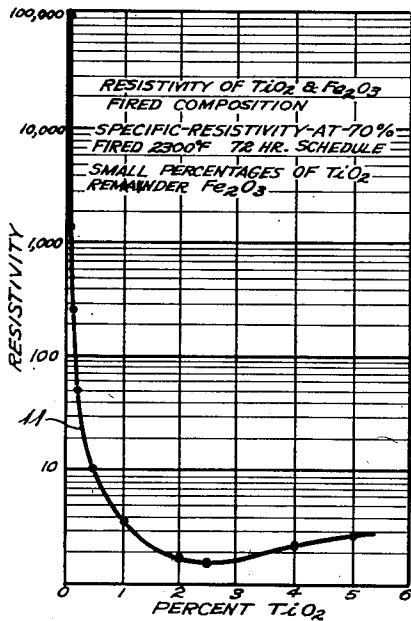
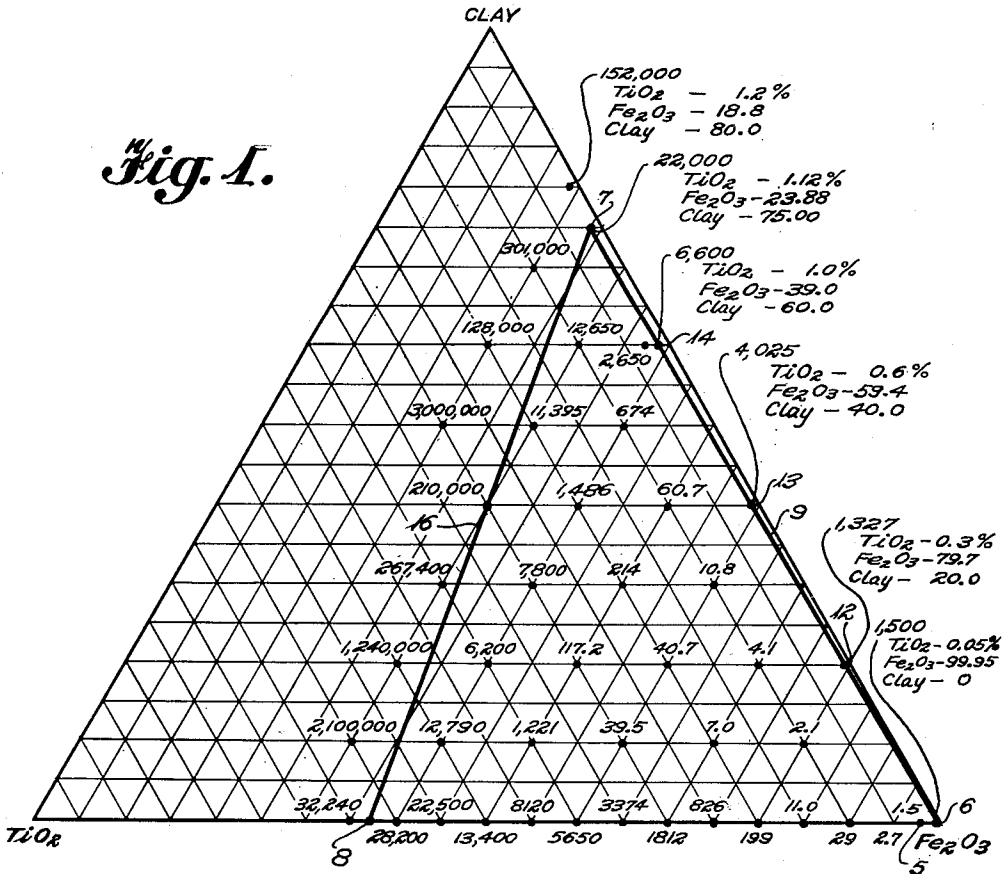
April 1, 1952

P. H. SANBORN
ELECTRICAL CONDUCTOR

2,590,894

Filed Sept. 20, 1949

3 Sheets-Sheet 1



INVENTOR

Paul H. Sanborn

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3 Sheets-Sheet 2

Fig. 4.

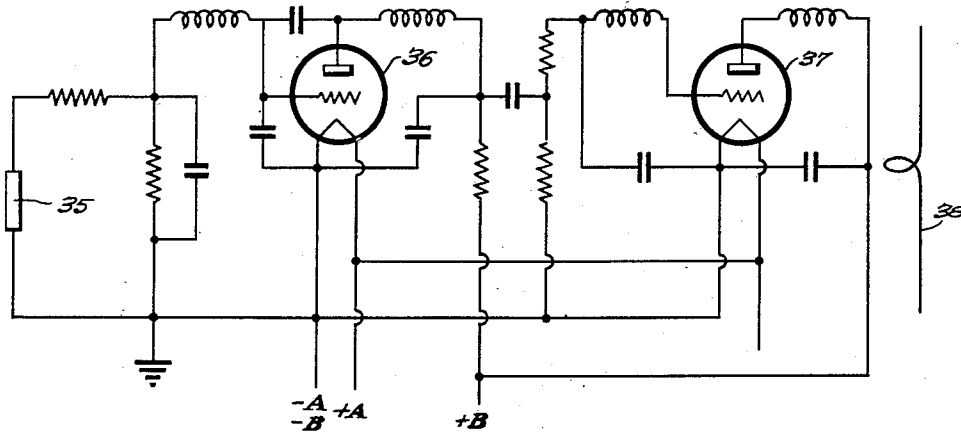


Fig. 5.

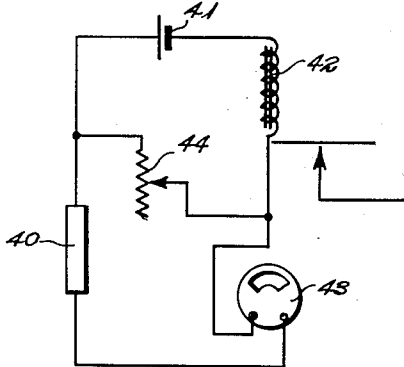


Fig. 6.

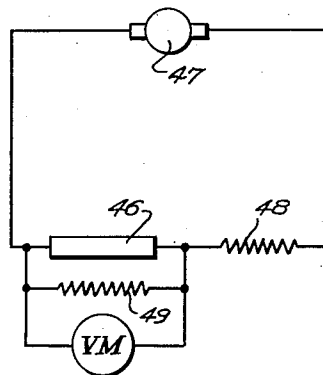
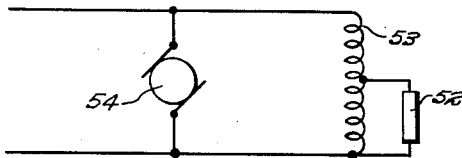


Fig. 7.



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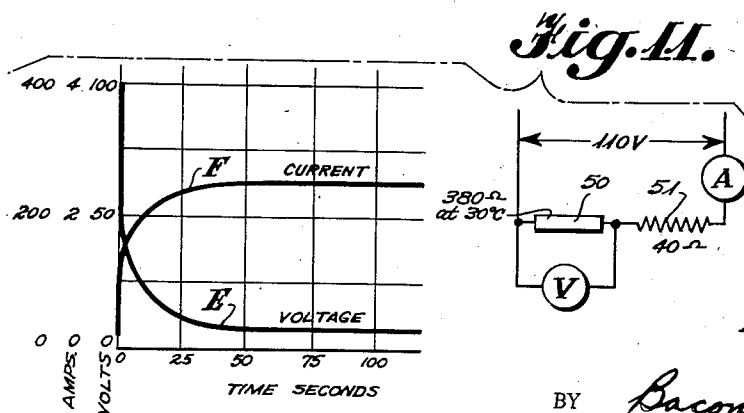
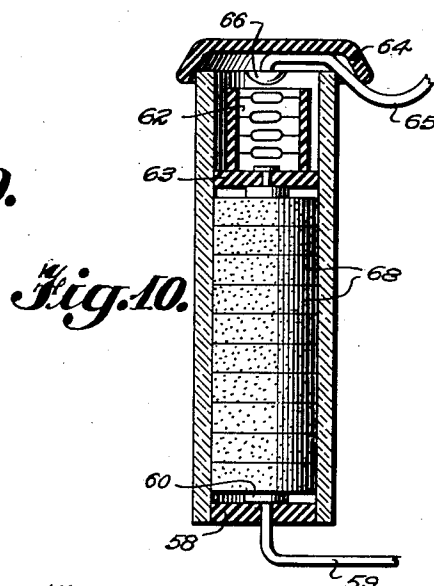
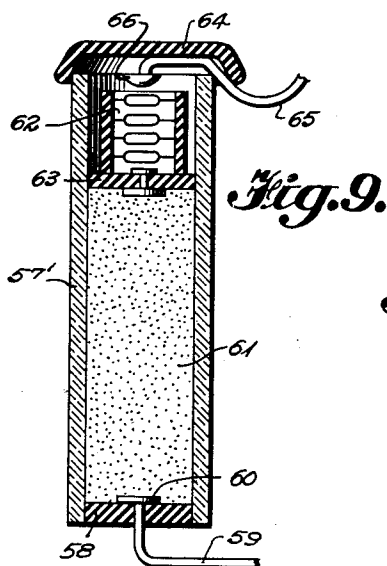
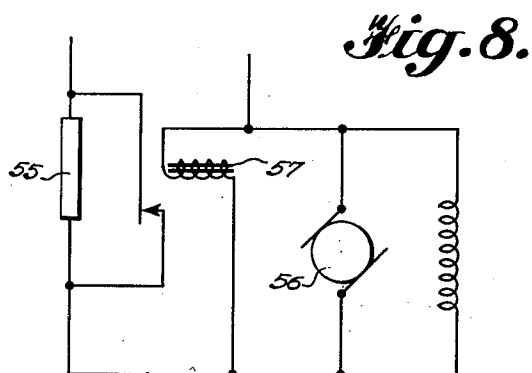
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3 Sheets-Sheet 3



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UNITED STATES PATENT OFFICE

2,590,894

ELECTRICAL CONDUCTOR

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Application September 20, 1949, Serial No. 116,672

12 Claims. (Cl. 252-490)

1

This invention relates to electrical conductors, and more particularly, to ceramic oxide compositions containing oxides of iron and titanium and having electrical conducting properties.

The products of the present invention have high negative temperature coefficients of resistance and are, therefore, capable of being employed for a wide variety of applications in which ordinary resistance or conducting materials are not adapted. As disclosed in my copending application, Serial No. 116,671, filed of even date herewith, similar products may be produced in the form of conducting coatings which may be applied to insulator bodies. Such conducting coatings include glass-like compositions having high mechanical strength. When applied to portions of electrical porcelain insulators employed on high voltage alternating current transmission lines so as to contact the conductor and, preferably also, the supporting member of the insulator, the conducting coatings or glazes reduce the discharges causing radio interference. The glass-like glazes may have mechanical properties, surface gloss and moisture imperviousness equal to ordinary insulating glazes conventionally employed on electrical porcelain insulators.

It is known that a number of metal oxides have conducting properties which vary according to the degree of oxidation or oxygen content. In general, the lower the degree of oxidation, the greater the conductivity. At the higher states of oxidation, for example, states of oxidation approaching those corresponding to ferric oxide or titanium dioxide, conduction is negligible. It is with the greatest difficulty that uniform conducting materials can be produced utilizing oxides in lower states of oxidation such that their conductivity is determined by their oxygen content. Such oxides are usually molded and heated to produce a dense mass. The degree of oxidation is determined by the oven or furnace atmosphere surrounding the oxides. The atmosphere during firing must be reducing or oxidizing to the exact degree required to produce the specific resistivity desired. Slight variations produce great changes in specific resistivity. In addition to the difficulty in maintaining the proper furnace atmosphere, the firing temperature and the time of heating also produce variable results. As the temperature is increased the mass becomes more dense so that the furnace gases can no longer penetrate it and the reactions occur at the exposed surfaces. The final products do not exhibit stable electrical characteristics because their oxygen content is not that which exists at the most stable state of

2

the oxides and during operation in electrical circuits, there is a trend toward higher values of resistance, particularly if the current is sufficient to produce appreciable heating. Furthermore, most oxides produce rather high values of specific resistivity.

It is known that either ferric oxide or titanium dioxide alone when heated under conditions in which oxygen is present during the entire heating period, produce materials of very high resistivity, i. e., negligible conductivity. In accordance with the present invention, it has been discovered that, if these two oxides are mixed in the proper proportions and fired in an oxidizing atmosphere, materials are produced which have conductivities which are millions of times greater than the conductivities of either of these oxides fired alone under the same conditions. The oxidizing atmosphere is that prevailing in commercial ceramic kilns in which free oxygen in excess of that necessary for the combustion of the fuel is present.

It has been determined from an investigation of the ferric oxide-titanium dioxide system that the composition of 2.5% titanium dioxide and 97.5% ferric oxide produces the lowest resistivity of any combination of these oxides. A specific resistivity of 1.5 ohm centimeters has been obtained with this composition prepared by pressing in steel dies and firing to 2300° F. on a 72 hour total cycle, whereas a 100% chemically pure ferric oxide composition or a 100% chemically pure titanium dioxide composition prepared in the same manner has a specific resistivity of millions of megohms. Within the range between 100% ferric oxide and 97.5% ferric oxide and 2.5% titanium dioxide there is an extremely rapid decrease in specific resistivity. There is tremendous reduction in resistivity between 100% ferric oxide and the composition 99.5% ferric oxide and 0.5% titanium dioxide. As the titanium dioxide is increased above 2.5% the specific resistivity increased slowly then rapidly until the specific resistivity of the composition 97.5% titanium dioxide-2.5% ferric oxide is 10^{14} ohm per cubic centimeter.

To explain the formation of semi-conductors of low specific resistivity from two oxides which normally have extremely high specific resistivity, it is advisable to consider the atomic structure and the behavior of electrons in accordance with the modern theory of solids. Atoms of solids are bound together and form a crystal lattice. Each atom nucleus is surrounded by a number of electrons which have definite paths and energies.

Some electrons are bound and revolve around the nucleus. Other electrons are free and may jump from atom to atom. Metals or conductors, semi-conductors and insulators have energy states which are grouped into bands. The energy bands are derived from the atomic energy levels of free atoms. Each band consists of a large number of closely spaced energy levels. There is a single free electron in each level of a band. The allowed bands filled and empty are separated by ranges of energy containing no levels and are known as forbidden bands because they are not permitted to electrons. If the forbidden band is wide, the band structure is that of an insulator. If, however, this band is small and the gap in energy between the highest filled band and the lowest empty band is of the order of fractional electron volts, the material is a semi-conductor. Filled and empty bands separated by small forbidden regions is the band structure of an intrinsic semi-conductor. Conduction in intrinsic semi-conductors is by excited electrons jumping into the empty bands.

Extrinsic semi-conductors have band structures similar to that of insulators except that the forbidden region contains extra energy levels as the result of lattice imperfections or the presence of impurities. These extra energy levels in the forbidden region act either as donators or acceptors. At finite temperatures the donator level may pass on its electron to the empty band and in the process causes conduction. Similarly, an acceptor may accept an electron from the filled band. The loss of the electron leaves an empty level in the formerly filled band. Conductivity may result from a few electrons in a normally empty band or a few vacancies in a normally filled band. It is convenient to consider the vacant levels as holes in a nearly full band. These holes act as positive charged electrons.

Most extrinsic semi-conductors become intrinsic semiconductors at elevated temperatures. Heat excites the electrons in intrinsic conduction. Extrinsic semi-conductors are most useful because they can be produced with low resistance at ordinary temperatures. Extrinsic semi-conductors are of two types:

- (1) "N" type semi-conductors which conduct principally by electrons in a nearly empty band;
- (2) "P" type semi-conductors which conduct principally by holes in a nearly filled band.

The introduction of extra discrete energy levels in the forbidden region account for the conductivity and determine the type of semi-conductor whether "N" or "P" type. The titanium dioxide-ferric oxide semi-conductor contains titanium dioxide as the impurity. It is the titanium dioxide which causes the distortion of the ferric oxide lattice and produces changes in the inherent physical structure and the electrical and mechanical forces. The distortion produces the levels between the filled and empty bands.

"N" type semi-conductors have characteristics which differ from those of the "P" type. If a metal connection is made to each end of a rod of the semi-conductor material to produce a thermocouple and if one junction is heated, the polarity of the junctions is characteristic of the type of semi-conductor. If the lead from the hot junction is positive and the lead from the cold junction is negative, the semi-conductor is of the "N" type. Should the hot junction be negative and the cold junction be positive, the semi-conductor is of the "P" type.

A ferric oxide-titanium dioxide semi-conductor

as an element of a thermocouple with copper, platinum, gold and other metals as the metallic element has positive polarity at the hot junction and therefore exhibits the characteristics of an "N" type semi-conductor.

The point contact rectification properties of a semi-conductor are also an indication of the type of semi-conductor. If the current flow is greater when the cat whisker or point contact is positive than when negative, the semi-conductor is of the "N" type. If greater current flows when the point contact is negative, the semi-conductor is of the "P" type.

As a point contact rectifier with a ferric oxide-titanium dioxide semi-conductor, the greatest current flow is with the point contact made positive. The ferric oxide-titanium dioxide semi-conductor, therefore, is of the "N" type.

Since the conductivity of a semi-conductor is the result of the introduction of extra energy levels in the forbidden zone as the result of lattice imperfections, impurities or the effect of the impurities in producing lattice imperfections, X-ray diffraction patterns were made of the ferric oxide-titanium dioxide semi-conductor materials and of pure ferric oxide to observe the changes. Finely ground crystal powder produces a diffraction pattern of sharp lines, the position and intensity of which are completely characteristic for each pure single compound. When a crystalline substance is exposed to a fine beam of monochromatic X-radiation, a series of secondary reflected beams emerge which have definite spacings and intensities depending upon the atomic structure of the substance irradiated. These beams are recorded on a photographic film. The X-ray reflections from crystalline planes are critical and emerge at specific angles only. The reason for this is that the crystal is an orderly arrangement of particles in a three-dimensional lattice. The actual distance between planes may be determined from the X-ray diffraction pattern. The interplanar distances calculated from the X-ray diffraction pattern have been determined for thousands of chemical compounds and minerals. These data have been indexed in a card file system "data cards for the identification of crystalline materials," available from the American Society for Testing Materials. These cards contain the interplanar distance ("d") in angstrom units. Determinations have been made upon selected compositions as follows:

Sample 1— 100% Ferric Oxide, C. P. Grade	Sample 2— 97.5% Ferric Oxide, 2.5% Titanium Di- oxide	Sample 3— 66.6% Ferric Oxide, 33.4% Titanium Di- oxide
2.69	2.635	14.98
2.51	2.475	13.24
2.21	2.16	2.76
1.84	1.813	2.46
1.72	1.673	2.23
1.475	1.469	1.685
-----	1.440	1.872
-----	1.300	1.735
-----	-----	1.655
-----	-----	1.552

¹ Lines of titanium dioxide.

The samples were fired in the same kiln and at the same time at 2300° F. on a 72 hour schedule. The spacings ("d") of the sample composed of 100% C. P. ferric oxide are identical with the ASTM card index for ferric oxide. It will be observed from the spacings of sample No. 2 that they are similar to those present in sample No. 1 with the exception that sample No. 2 has smaller

lattice spacing, indicating a compression of the lattice. The conclusion is that the 2½% of titanium dioxide produces a compression of ferric oxide lattice or lattice imperfection. Titanium dioxide plays the role of an impurity. Sample No. 3 containing a larger amount of titanium dioxide shows an expansion of the lattice of ferric oxide. The spacings are compressed with 2½% titanium dioxide and larger amounts produce an expansion of the lattice.

The distortion of the ferric oxide lattice by the titanium dioxide occurs even if large amounts of other ceramic materials are employed. For example, a composition containing clay as well as ferric oxide and titanium dioxide was prepared and fired under the same conditions as the above samples.

Sample 4—	
50% Ferric oxide, 10% Titanium dioxide, 40% Ball clay	
	4.10
	3.475
	2.70
	2.52
	2.215
	2.14
	1.843
	1.690
	1.520
	1.460

1 Lines of ferric oxide.

By comparison with Example 1 it will be observed that the lattice spacings of the ferric oxide show a slight expansion.

The electrical conductors of the present invention therefore comprise fired mixtures of ferric oxide and titanium dioxide. In general, the materials having the lowest resistivity are those which contain only pure ferric oxide and titanium dioxide and have a small amount of the titanium dioxide relative to the ferric oxide. For example, in compositions containing only ferric oxide and titanium dioxide, the lowest resistivity occurs at about 2.5% titanium dioxide. Decreasing the percentage of titanium dioxide causes the resistivity to increase and after the amount of titanium dioxide has been decreased to approximately 0.05%, further decrease in the titanium dioxide causes the resistivity to increase very rapidly. Also, increasing the amount of titanium dioxide causes the resistivity to gradually increase until relatively large percentages of titanium dioxide are reached, after which a still further increase of titanium dioxide causes a large increase in resistivity.

Substantially any other ceramic materials, i. e., any other oxides or mixtures of oxides ordinarily employed in making ceramic materials may be added to the ferric oxide-titanium dioxide compositions just discussed. Such ceramic materials may be, for example, various silicates such as aluminum silicate as well as silica, alumina, zirconia, and various fluxes such as alkali metal or alkaline earth metal oxides, zinc oxide, borax, boric acid, etc. The effect of adding such materials is primarily that of adding a diluent. The resistivity of the composition at first gradually increases as the amount of other ceramic materials is increased. As greater amounts of such materials are added to the composition, however, the rate of increase of resistivity becomes greater and a point is reached at which the resistivity rapidly increases. The point at which this oc-

curs depends upon the ratio of titanium dioxide and ferric oxide, it being possible to add greater amounts of the other ceramic materials when the ratio of titanium dioxide to ferric oxide is low, i. e., when the percent of titanium dioxide based upon the total amount of ferric oxide-titanium dioxide present is between approximately 1% and 10%. Various admixtures of ceramic materials can be employed in order to improve the physical characteristics of the conducting material. That is to say, mixtures of pure ferric oxide and titanium dioxide, when fired, may not have the desired structural strength but by adding silicates or other of the known ceramic materials in accordance with well known ceramic formulas, resulting products having the desired physical properties can be produced.

All of the conducting materials of the present invention have a rather high negative temperature coefficient of resistance. Those containing pure ferric oxide and titanium dioxide as well as those containing ceramic materials such as silicates, silica, light metal oxides, etc., all have substantially the same negative temperature coefficient of resistance. Compositions of this nature will have their conductivity increased approximately 10 times when the temperature is increased from 32° F. to 212° F., the negative temperature coefficient of resistance increasing as the temperature is increased, and decreasing as the temperature is decreased.

The addition of heavy metal oxides added to either the conducting materials containing pure ferric oxide and titanium dioxide or to compositions containing other ceramic oxides will ordinarily change the temperature coefficient of resistance. For example, the addition of small amounts of copper oxide will increase the negative temperature coefficient of resistance while the addition of small amounts of chromium oxide will decrease the negative temperature coefficient of resistance. Other heavy metal oxides, for example, oxides of vanadium, manganese, cobalt and nickel as well as those of tungsten, molybdenum and bismuth are also useful in compositions of the present invention, for example, oxides of the latter two metals are useful for reducing the fusion point of the compositions without using the basic oxides previously mentioned although they as well as the other heavy metal oxides may also be employed in conjunction with the basic oxides or other fluxes discussed above. Low resistance, low fusibility silica-free compositions may be produced by using molybdenum or bismuth oxides or both. In general, the amount of heavy metal oxides other than ferric oxides and titanium dioxide incorporated into the conductor composition will not exceed the amount of titanium dioxide present, or in any event, will not exceed approximately 50% of the ferric oxide. Although certain of the heavy metal oxides, for example copper oxide, are "P" type semi-conductors, their employment in ferric oxide-titanium dioxide semi-conductors in the amounts mentioned does not alter the "N" type conducting characteristics.

It is therefore an object of the present invention to provide an improved electrical conducting material having any desired resistivity, including a low resistivity, in which the conducting materials comprise a vitrified mixture of oxides which separately are insulating materials.

Another object of the present invention is to provide an improved ceramic electrical conducting material having any desired resistivity in-

cluding a low resistivity and also having a negative temperature coefficient of resistance.

Another object of the invention is to provide an improved resistor element having a high negative temperature coefficient of resistance.

A further object of the invention is to provide a process of making a ceramic electrical conducting material having a high negative temperature coefficient of resistance.

Other objects and advantages of the invention will appear from the following description of preferred embodiments thereof given in connection with the attached drawing, of which:

Fig. 1 is a triaxial diagram showing compositions suitable for conducting materials including resistor elements;

Fig. 2 is a graph showing the resistivity of fired compositions made up of pure titanium dioxide and ferric oxide for small percentages of titanium dioxide;

Fig. 3 is a schematic diagram showing a simple temperature measuring system including a resistor element in accordance with the present invention;

Fig. 4 is a schematic diagram showing a resistor element of the present invention for controlling the frequency of modulation of a radio frequency wave for temperature indication at a distance;

Fig. 5 is a schematic diagram illustrating the employment of a resistor element in accordance with the present invention for temperature control of relays;

Fig. 6 is a schematic diagram illustrating voltage regulation by a resistor in accordance with the present invention;

Fig. 7 is a view similar to Fig. 6 showing a different type of voltage regulator;

Fig. 8 is a schematic diagram showing a motor starting arrangement using a resistor in accordance with the present invention;

Fig. 9 is a diagrammatic section of a lightning arrester showing the employment of the resistivity of the material of the present invention therein;

Fig. 10 is a view similar to Fig. 9 showing a modified lightning arrester; and

Fig. 11 is a curve showing the relation between time, voltage and current in a typical resistor heated by current flowing therethrough.

For purposes of illustrating the present invention, the resistivity characteristics of various compositions including three components, namely, titanium dioxide, ferric oxide and clay, have been shown in the form of a triaxial diagram in Fig. 1. Substantially pure titanium dioxide and ferric oxide were employed but the clay was a mixture of ball clay and bentonite, both of which contain substantial amounts of materials other than aluminum silicates. In all compositions containing clay, 5% of the total composition was bentonite, which is an extremely plastic material and was used to give good ceramic properties to the compositions having low clay content, and the remainder of the clay in each composition was ball clay. The particular ball clay employed contained 1.6% titanium dioxide, and 1.5% ferric oxide as impurities and the compositions of the triaxial diagram are corrected to show the actual amount of titanium dioxide and ferric oxide therein. This, in conjunction with improved technique in making electrical contact with the fired compositions, results in general, in lower resistivities for a given composition than those reported in my

copending application Serial No. 408,400, filed August 26, 1941, now abandoned. In all cases, the compositions were fired under the same conditions, i. e., at 2300° F. on a 72 hour total cycle including heating and cooling. The resistivities are given in ohms per centimeter cube at 70° F., i. e., the specific resistivity at 70° F.

In Fig. 1, the point 5 indicates a composition containing no clay but containing 2.5% titanium dioxide and 97.5% ferric oxide. This composition provided a resistance of approximately 1.5 ohms per centimeter cube which is approximately the lowest resistance which can be obtained employing titanium dioxide and ferric oxide. Any substantial change in this composition increases the resistivity. In general, the lowest resistivities are obtained by employing a temperature during firing which is just sufficient to vitrify and an extended time of treatment at this temperature so as to insure a uniform composition throughout the sample. A firing temperature lower than 2300° F. would produce a series with higher individual resistivities while a higher temperature would produce, in general, a lower resistivity for each of the samples containing clay, providing over-firing with resulting devitrification does not occur. The compositions containing titanium dioxide and ferric oxide without the addition of clay may have organic binding agents, such as waxes or similar bonding materials added thereto to improve the working properties but such bonding materials are burned out during firing and have no appreciable effect upon the final resistivity. However, all of the compositions of the triaxial diagram were produced by merely pressing dampened powder made up of the mixed ferric and titanium oxides and clay in steel dies prior to firing.

After reaching the maximum firing temperature the rate of cooling affects the final resistivity. If the cooling is rapid, the resistivity is lower than if the rate of cooling is slow.

The fired samples were provided with terminals by application of metal compounds of the type used for ceramic decoration. Commercial gold was employed in producing the samples, but platinum and silver as well as gold have also been used and have proven satisfactory providing they are fired to the proper temperature since these materials usually contain a fusible layer on the semi-conductor if the firing temperature is too high. It will, of course, be understood that the ceramic compositions are first fired to the proper temperature, after which the ceramic metal is applied to provide terminals, and then the conducting elements again fired at a lower temperature. The rate of cooling following the metallizing operation has an effect upon the final resistivity in somewhat the same manner as the cooling following the original firing of the conducting bodies. The resistivity will be slightly lower if the rate of cooling is rapid. The reason for this effect is apparent when it is realized that the semi-conductor compositions have high negative temperature coefficients of resistance. Heating decreases the resistance while cooling increases the resistance. If the semi-conductor material is heated and cooled slowly it will have a value of resistivity corresponding to the final temperature. If, however, it is cooled rapidly, molecular rearrangement cannot take place rapidly enough and some of the characteristics imparted by higher temperatures are retained. It is not

difficult to produce successive batches having almost identical characteristics when the materials are subjected to similar conditions in the processing, particularly the temperature of firing and of the cooling cycles following firing and metallizing.

Referring again to Fig. 1, the useful ranges of compositions are approximately bounded by the lines joining the points 6, 7 and 8. These points are as follows:

- (6)—titanium dioxide 0.05%, ferric oxide 99.95%, clay 0.
- (7)—titanium dioxide 1.12%, ferric oxide 23.88%, clay 75%.
- (8)—titanium dioxide 63%, ferric oxide 37%, clay 0.

The line 9 connecting the points 6 and 7 is drawn approximately through the points at which a further decrease in the titanium dioxide content, i. e., a decrease in the ratio of titanium dioxide to ferric oxide will cause an extremely large increase in resistivity. This is illustrated in Fig. 2 in which the curve 11 represents resistivity in ohms per centimeter cube plotted against a small percentage of titanium dioxide, the remainder of the composition being ferric oxide. The resistivity was measured on samples fired at 2300° F. on a 72 hour schedule with ceramic gold terminals applied thereto as discussed above. A minimum point of resistivity was obtained at 2.5% titanium dioxide and the curve becomes substantially vertical at a composition containing 0.05% titanium dioxide. Similar curves can be drawn for each percentage of clay and their form is similar to that of Fig. 1. The percentage of titanium dioxide in the total composition which gives minimum resistivity will increase as the percentage of clay is increased and the ratio of titanium dioxide to ferric oxide which gives minimum resistivity will also increase. Similarly, the percentage of titanium dioxide in the total composition, at which the resistivity curve becomes substantially vertical for decreasing amounts of titanium dioxide, will increase, but as stated above, the shape of the curve for each percentage of clay will be very similar to that of Fig. 2. Points 12, 13 and 14, which are close to the point at which the resistivity begins to increase rapidly, have also been plotted on the triaxial diagram and the straight line 9 has been drawn therethrough. It will be noted that this line is close to the zero titanium dioxide axis of the triaxial diagram.

In a similar manner, straight line 16 has been drawn to connect points 7 and 8 on the triaxial diagram. This line passes through the points which closely approximate those at which the resistivity of the compositions rapidly increases as the percentage of titanium dioxide is increased, i. e., the ratio of titanium dioxide to iron is increased while the amount of clay is maintained constant. This can be seen qualitatively from the triaxial diagram, as in general, the points to the left of the line 16 indicate very high resistance as compared with the points at the right of the line 16. That is to say, curves showing resistivity plotted as ordinates against percentages of titanium dioxide in the total composition as abscissa when the amount of clay is maintained constant, become substantially vertical at points adjacent the line 16.

In compositions for producing conducting elements usable as negative temperature coefficient

resistors, etc., the amount of titanium dioxide in the total composition ranges from approximately 0.05% to 63%, the amount of ferric oxide ranges from approximately 23.88% to 99.95% and the amount of other ceramic oxides, such as those contained in clay, ranges from approximately zero to 75%. In addition to never being greater than 63%, the percentage of titanium dioxide in the ceramic compositions should not be greater than 4.7165 times the percentage of ferric oxide minus 111.51% and in addition to never being less than 0.05%, the percentage of titanium dioxide should not be less than 1.4560% minus 0.01407 times the percentage of ferric oxide. Also, in addition to never being greater than 75% of the composition, the percentage of other ceramic oxides, such as those contained in clay, should not be greater than 98.544% minus 0.9859 times the percentage of ferric oxide.

The above limits completely define the area on the triaxial diagram bounded by the lines 9 and 16 and the axis of the diagram for zero amount of clay. The compositions included within the limits above expressed will all have a specific resistivity less than approximately 30,000 ohms per centimeter cube. A small increase in the ratio of titanium dioxide to ferric oxide near the line 16 will cause a rapid increase in specific resistivity and the same is true of a small increase in the ratio of clay to the total amount of titanium dioxide and ferric oxide. Similarly, a small decrease in the ratio of titanium dioxide to ferric oxide near the line 9 will cause a large increase in specific resistivity.

The resistivities reported on the triaxial diagram of Fig. 2 are approximately the minimum resistivities which applicant has been able to obtain using the best techniques known to him. Variations in the firing procedure including temperature and heating and cooling periods, may be employed to somewhat modify the resistivities, but in any event, the boundaries represented by lines 9 and 16 on the triaxial diagram pass very closely to the points at which variations in the composition cause a rapid increase in resistivity. This is true irrespective of whether the other ceramic oxides are the clay (aluminum silicate) of the triaxial diagram or other ceramic oxides such as silica itself, zirconium oxide, potassium oxide, sodium oxide, etc., or whether other heavy metal oxides such as chromium, copper, cobalt, manganese, etc., are present. An example of how changing the type of ceramic material other than the active oxides will vary resistivities of the composition even though the total amount of such materials is maintained constant and the amount and types of active oxides are maintained constant, the following table is given:

	Samples—			
	No. 1	No. 2	No. 3	No. 4
Titanium dioxide.....	10	10	10	10
Ferric oxide.....	65	65	65	65
Ball clay.....	20	5	—	—
Zirconia.....	—	15	25	—
Alumina.....	—	—	—	25
Bentonite.....	5	5	—	—
Resistivity.....	8.3	8.3	8.9	14.1

Here the zirconia and silicates together produce a lower specific resistivity than zirconia alone while zirconia alone produces a lower specific resistivity than alumina alone. The samples were prepared under identical conditions.

The titanium dioxide-ferric oxide semi-conductors have negative temperature coefficients which increase at lower temperatures and decrease at higher temperatures. Most of these semi-conductors containing oxides and silicates as diluents show 2% to 3% change in resistivity per degree C. at 25° C. Some heavy metal oxides as diluents product variations from these values. Compositions containing copper oxide, which reduces the firing temperature if present in appreciable amounts, increases the change per degree while chromium oxide decreases the change per degree. While copper oxide is a "P" type semi-conductor its use in a titanium dioxide-ferric oxide does not alter the "N" type characteristics.

Other materials than the oxides may, of course, be employed in producing the original composition so long as these materials are converted to the oxides during the firing operation. Such other materials are, for example, hydroxides and carbonates as well as the silicates of magnesium, aluminum, zirconium, etc. In this connection, the silicates are considered to be oxides. In addition, a wide variety of fluxes, such as calcium oxide, sodium or potassium oxides or compounds of silicates of alumina with sodium, potassium or calcium, such as feldspar, may be employed as well as other light metal oxides such as zinc oxide. In fact, substantially all of the materials conventionally used in ceramics, either to form the body of the fired article or as a flux for lowering its melting point may be employed in the titanium dioxide-ferric oxide compositions of the present invention.

The heavy metals employed in combination with titanium in accordance with the present invention are preferably added in the oxide form at their highest degree of oxidation or at least in a state of oxidation greater than the lowest. However, any compounds of these metals which are converted into the oxide during firing under oxidizing conditions may be employed. The same is true of the light metal or non-metal oxides employed as part of the composition. Thus in general, the carbonates are suitable and in some instances, the halides. For example, with iron any of the oxides can be employed if care is taken to oxidize the same during firing. Also the sulfates and chlorides may be employed as well as ferrous ammonium sulfate. With titanium the other oxides such as Ti_2O_3 and also titanium sulfate may be employed instead of titanium dioxide and naturally occurring titanium ores such as rutile can also be employed. It is apparent that the hydroxides of any of the metals may likewise be employed as the water of crystallization is driven off during firing. Furthermore, natural ores containing iron or other heavy metal oxides and titanium may be employed with or without suitable additions of oxides to produce the desired ratio of titanium to other heavy metal oxide. Thus ilmenite which is a mixture of iron and titanium oxide, or joaquinite which is an iron titanium silicate, or titanite which is a calcium titanium silicate, may be employed. In general where the titanium is added in the form of an ore, for example, in combination with iron or silicon or other metals, the ratio of titanium to iron or other heavy metal oxide must be increased somewhat over those necessary with the individual oxide as the effectiveness of the titanium appears to depend somewhat upon its previous history. To illustrate this factor the following

composition was prepared, changing only the material containing the titanium dioxide:

Titanium dioxide	10.8
Ferric oxide	54.2
Ball clay	30.0
Bentonite	5.0

The following table shows the variations in resistance with the source of titanium dioxide:

Source	Resistance ohms per cm^3 at 70° F.
Rutile #1	48.4
Rutile #2	50.9
Ilmenite	53.8
Anatase	42.0

It will be apparent that anatase gives the lowest resistivity and that ilmenite in which the titanium occurs with iron, gives the highest resistance.

Resistance units in accordance with the present invention may be prepared by substantially any of the methods employed in producing ceramic bodies. The direct method of merely grinding materials together in a pebble or ball mill with sufficient water to make a slurry is preferred. After thorough mixing and grinding, the excess water may be removed by filter pressing or drying in the air or on plaster slabs. The resulting plastic mass may be pressed in dies or may be extruded into rods or tubes through proper sized dies commonly used in the ceramic industry. If plastic clays are not used, it is desirable to use organic binding agents known to the art, such as various waxes, dextrin, gum arabic and similar substances. The rods may then be dried and fired either before or after cutting into suitable lengths for resistance units. Alternatively, the resistor units may be dry pressed in which case the slurry from the pebble mill is dried to a lower moisture content than that necessary for extrusion. In proper condition the material will be a damp crumbly mass and in this state the material may be placed in steel or rubber molds and molded by pressure. It will be apparent that any of the usual pottery forming methods such as dry-pressing, extruding, casting, hot-pressing, or jiggering may be employed. It is possible also to produce conducting grains suitable for employment as resistance material in lightning arrestors in which case the mixture from the ball mill is substantially completely dried and the resulting hard material crushed and screened to obtain the proper grain size. The grains are then fired in a suitable container such as a fire clay crucible to the proper temperature.

It is also possible to fire a powdered mixture of titanium and iron oxides or such a mixture containing other materials as one or more of the other heavy metal oxides mentioned, which produces a composition having a rather high fusion point, to the proper temperature to produce conductivity and then pulverize the resulting mix. This powdered conducting material could be then mixed with low temperature ceramic fluxes and fired again at low temperatures. This produces conducting articles at low firing temperatures. Such fluxes may be lead oxides, kryolith, borax, boric acid, and other materials now used in the production of porcelain enamel.

The correct temperature for firing any of the compositions above discussed is that which will

cause vitrification of the material without substantial devitrification during the time which the compositions are subjected to such temperature. Best results are ordinarily obtained by employing the longest firing cycle which is commercially feasible and the lowest firing temperatures which will cause vitrification under such conditions. Somewhat higher temperatures can, however, be employed with a correspondingly shortened firing cycle. Mixtures of substantially pure ferric oxide and titanium dioxide will usually be fired at a temperature in the neighborhood of 2300° F. but with compositions containing substantial amounts of other ceramic materials, the nature of and proportions of such other materials may be varied as discussed above so as to secure firing temperatures ranging between approximately 1500° and 2500° F. while still producing fired compositions having relatively low specific resistivities. That is to say, substantially any known or suitable ceramic materials or mixtures of ceramic materials which can be molded and then fired to produce bodies of adequate mechanical strength can be employed instead of the clay shown for illustrative purposes in the triaxial diagram. Such ceramic compositions will, in general, produce fired products of extremely high specific resistivity in the absence of both titanium dioxide and ferric oxide when fired under oxidizing conditions producing a state of oxidation equivalent to ferric oxide or titanium dioxide but when admixed with ferric oxide and titanium dioxide in the proportions given as to clay on the triaxial diagram and fired under such oxidizing conditions, specific resistivities of the same order as those shown are obtained. Although mixtures of substantially pure ferric oxide and titanium dioxide produce fired bodies of relatively low specific resistivity useful for many purposes, resistors in accordance with the present invention will, in general, contain at least 10% of other ceramic materials to either provide increased workability of the composition before firing or increased mechanical strength after firing. By employing glass-forming materials, such as silica and a flux for the other ceramic materials, a glass or glass-like material having a relatively low specific resistivity can be produced upon firing. In such glasses the amount of other ceramic materials will ordinarily be at least 40%.

Various methods may be employed for insuring effective connection between the ends of the resistor units and resistor leads. For resistor elements having a low enough resistance to carry an electroplating current, conducting metals such as copper, nickel, tin, chromium, cadmium, etc., may be electrically plated upon the ends of the resistor unit. For all resistors including high resistance units metal may be sprayed upon the ends of the resistor units by any of the metal spraying processes known to the art. Another method particularly useful for precision resistors is to coat the ends of the resistor elements with ceramic liquid gold, platinum or other noble metal such as is used to decorate dishes. This material may be painted on the ends of the resistors or the resistors dipped therein and allowed to dry. By heating to approximately 1500° F., in the case of platinum, the platinum is reduced to metallic form and may then, if desired, be coated or plated with a conducting metal such as copper or silver. Resistor leads may then be soldered or clamped against the conducting metal on the ends of the resistor units and if desired

the entire resistor unit including the ends of the leads adjacent the resistance material may be imbedded in insulating material such as thermoplastic or thermosetting synthetic resins, for example, bakelite. If the leads and conducting metals on the end of the resistors have a sufficiently high melting point the entire resistor element including the ends of the leads adjacent the resistor may be dipped in a low melting point non-conducting glaze and again fired to provide resistors completely encased with glaze or glass-like insulating material.

A simple temperature measuring circuit is shown in Fig. 3 in which a resistor 32 is connected in series with a battery 33 and a current measuring instrument 34. The current measuring instrument 34 is preferably a micro-ammeter or milliammeter so as to operate with a low current in order that the current flowing through the resistor 32 has no appreciable heating effect upon the resistor. By applying a constant voltage across the resistor and meter 34 by means of a battery 33 or similar source of electromotive force the deflection of the meter 34 can be made a substantial straight line function of temperature over a relatively wide range and the meter may be calibrated directly in temperature units. By employing a resistor 32 which has a resistance large in comparison with the resistance of the rest of the circuit, the resistor may be located at a distance from the meter 34 to give remote temperature indications. For example, such a system can be employed for measuring temperatures at the tops of mountain peaks with the meter positioned at the base thereof. Such an arrangement may also be employed for such temperature indications as the water or oil temperature of motors in automobiles and airplanes. It will be apparent that the meter 34 can be a recording as well as an indicating instrument and that other factors such as the voltage drop across the resistor 32 when it is placed in series with another resistor or the voltage drop across such other resistor to indicate temperature. Another type of temperature measuring or indicating system is shown in Fig. 4 in which a resistor 35 of the type heretofore described is employed to vary the frequency generated by a tube 36 connected as an oscillator which frequency in turn modulates the output of a radio frequency oscillator 37 to provide a radio frequency voltage modulated with a lower frequency which varies with the temperature of the resistor 35. The tube 36 is shown connected as a relaxation oscillator but it is apparent that other types of oscillator circuits whose frequency can be made a function of resistance can be employed. The radio frequency from such a system as that shown in Fig. 4 may be radiated by an antenna 38 to form a transmitter. Such a transmitter may be carried by a free balloon employed in meteorography or may be positioned at remote points upon the ground and the signal picked up by a suitable receiving system by which the signal is demodulated and applied to a frequency meter or recorder which may be calibrated in temperature units.

As shown in Fig. 5 a resistor 40 having a high negative temperature coefficient of resistance may be employed for temperature control of relays, for example, a resistor 40 may be connected in series with a source of voltage 41, a relay coil 42, and if desired, a current measuring instrument 43 calibrated in temperature units. Upon increase in temperature the current through the resistor 40 and relay coil 42 increases until the relay closes. Adjustment of the closing temperature may be

made by varying the voltage 41 or the resistance of a variable resistor 44 in parallel with the temperature responsive resistor 40. It is apparent that the resistor 44 could be placed in series with the resistor 40, and that for relay closing upon a decrease of temperature the resistor 40 could be placed in parallel with the relay 42. The temperature responsive resistor of the present invention may also be employed for voltage regulation for either D. C. or A. C. currents in which case the thermo-responsive resistor 46 (Fig. 6) may be placed in series with the source 47 and a ballast or limiting resistor 43 which is preferably of a metallic type having a positive temperature coefficient of resistance. The voltage to be regulated is shown as applied across a load in the form of a resistance 49. Upon increase of voltage at the source 47 the increased current through the resistor 46 increases the temperature thereof to lower the resistance of the resistor 46 thus increasing the current through the resistor 43 and causing greater drop across the resistor 43 to lower the voltage across the resistor 46. If the load 49 is decreased to take increased current the voltage drop across the resistor 43 increases to decrease the voltage drop across the resistor 46 thus allowing the temperature of the resistor 46 to decrease and increase its resistance causing the voltage drop across the resistor 46 and the load 49 to increase. The opposite effect is produced upon increase of the load 49 so that the circuit shown tends to maintain the voltage across the load 49 substantially constant.

Reference is made to Fig. 11 to illustrate the relation between time and current and voltage of a typical resistor of the present invention heated by current flowing therethrough. As shown in the circuit of this figure, a resistor 50 having a resistance of 380 ohms at 39° C. was connected in series with a wire wound resistor 51 having a resistance of 40 ohms across a source of 110 v. The curve shows the drop in voltage across the resistor 50 after the voltage was applied and the curve F shows the increase in current. Under these conditions the value of resistance of the resistor 50 dropped from 380 ohms to approximately 2.5 ohms, or to about $\frac{1}{150}$ of its original value. By varying the physical size of the resistor relative to its resistance at a given temperature, the time for a given temperature, the time for given resistance drop can be varied within wide limits. Since the resistors of the present invention can withstand high temperatures approaching their firing temperatures as well as low temperatures such wide changes in resistance as above described can be utilized.

The thermo-responsive resistor of the present invention may also be employed for voltage regulation of generators. As shown in Fig. 7 the thermo-responsive resistor 52 may be connected across all or a portion of the field 53 of a generator 54. If the voltage of the generator 54 tends to increase, current flowing through the resistor 52 increases its temperature and lowers its resistance to more effectively shunt the field 53 to decrease the voltage of the generator 54. By employing a resistor 52 of sufficient size to radiate effectively the heat produced by current flowing therethrough without materially increasing its temperature the resistor 52 may be employed to regulate the voltage of the generator 54 in accordance with the temperature of the atmosphere in which the resistor 52 is positioned. Thus the resistor 52 can be employed to increase the charging rate of an automobile battery as the atmospheric

temperature decreases so as to automatically increase the rate of charging an automobile battery in the winter and decrease this rate in summer. In such a system the resistor 52 should be located at a point remote from the engine so as to not be subject to engine heat.

Referring to Fig. 8, the thermo-responsive resistor 55 may be employed for motor starting. In the diagram shown the resistor 55 is in series with the motor 56 and has a relatively high resistance at ordinary temperatures. Thus a relatively low voltage is initially applied to the motor 56. Current flow through the resistor 55 gradually decreases the resistance thereof, thus decreasing the voltage drop across the resistor and increasing the voltage across the motor 56. When the voltage across the motor increases to a predetermined value the relay 57 operates to short-circuit the resistor 55, at the same time completing a locking circuit for holding the relay 57 energized during running of the motor. The resistors of the present invention may be built of relatively large sizes capable of standing extremely high temperatures, that is, any temperature below the relatively high firing temperatures employed in producing the resistor and can be employed in accordance with the circuit of Fig. 8 to start relatively large motors of either the direct current or alternating current type as well as to gradually apply voltage to any other type of equipment. It will be apparent that conventional starting resistors may be connected in parallel with the resistor 55 and the resistor 55 made of relatively small size and merely employed to provide a time delay before shorting out the main resistor. A series of resistors can of course be employed with appropriate time delay resistors of the present invention and relays for cutting out a series of main resistors in steps. It will also be apparent that the resistors of the present invention may be employed as heating elements even for high temperature operations particularly if they contain substantial amounts of refractory oxides such as zirconia or alumina.

Another important application of the resistance material of this invention is in lightning arresters. As shown in Fig. 9, such a lightning arrester may comprise a tube 57' of insulating material such as porcelain closed across its bottom with a plug of insulating material 58 through which a conductor 59 extends terminating in a contact member 60. The tube 57' may be partially filled with grains of resistance material 61 having a high negative temperature coefficient of resistance and in the upper portion of the tube 57' a series of spark gaps 62 may be provided and separated from the resistance grains by an insulating barrier 63. The entire lightning arrester may be provided with a cap of insulating material 64 made of porcelain or like material, with a conductor 65 extending therein and having a terminal 66 forming part of the spark gap 62. As shown in Fig. 10, discs 63 of resistance material having a high negative temperature coefficient of resistance may be substituted for the grains 61. Otherwise the lightning arrester structure may be similar to that of Fig. 9.

Resistance material such as the grains 61 of Fig. 9 or the discs 63 of Fig. 10 have a relatively high resistance at ordinary temperatures and are in series with the spark gaps so that a relatively high voltage must be applied between the contacts 60 and 64 before any current flows through the arresters. When surges due to lightning or other causes appear on the power line current flows through the arresters and the en-

ergy of the surges is dissipated as heat. The resistor material for lightning arresters should be capable of withstanding high temperatures and compositions including substantial amounts of such refractory oxides as zirconia or alumina in addition to titanium oxide, another oxide of a heavy metal and a plastic binder such as clay are preferred.

The resistors of the present invention have various other important applications such as compensation for frequency drift in oscillator circuits and intermediate frequency application circuits of radio apparatus due to changes in temperature, and compensation for variations in temperature for the cold junctions of thermocouples. They may also be employed in Wheatstone bridge resistance thermometers, fire alarms, controlling the heating current in starting fluorescent lamps, etc. It will thus be seen that I have provided an improved conducting or resistance material prepared from inexpensive materials which are themselves substantially non-conducting. The improved conducting material can be made of low resistance and has a high negative temperature coefficient of resistance. The resistance and temperature coefficient of resistance at a given temperature can be varied within wide limits and the new material has a wide variety of uses.

This application is a continuation-in-part of my copending application Serial No. 408,400, filed August 26, 1941, which in turn is a continuation-in-part of my application Serial No. 328,322, filed April 6, 1940, both of said copending applications now being abandoned.

I claim:

1. An electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogeneous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 0 to 75% other ceramic oxides by weight, said other ceramic oxides being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the percentage of any heavy metal oxides other than said ferric oxide and said titanium dioxide not exceeding the percentage of said titanium dioxide, and in any said composition the percentage of titanium dioxide not being greater than that obtained by multiplying the percentage of ferric oxide by 4.7165 and then subtracting 111.51%, or less than that obtained by multiplying the percentage of ferric oxide by 0.01407 and subtracting the result from 1.4560% and the percentage of other ceramic oxides not being greater than that obtained by multiplying the percentage of ferric oxide by 0.9859 and subtracting the latter result from 98.544%.

2. An electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogeneous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 10 to 75% other ceramic oxides by weight, said other ceramic oxides being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the percentage of any heavy metal oxides other than said ferric oxide and said titanium dioxide not exceeding the percentage of said titanium dioxide, and in any said composition the percentage of titanium dioxide not being greater than that obtained by multiplying the percentage of ferric oxide by 4.7165 and then subtracting 111.51%,

or less than that obtained by multiplying the percentage of ferric oxide by 0.01407 and subtracting the result from 1.4560% and the percentage of other ceramic oxides not being greater than that obtained by multiplying the percentage of ferric oxide by 0.9859 and subtracting the latter result from 98.544%.

3. An electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogeneous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 10 to 75% other ceramic oxides by weight, said other ceramic oxides including other heavy metal oxides and being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the percentage of said other heavy metal oxides not being greater than the percentage of said titanium dioxide, and in any said composition the percentage of titanium dioxide not being greater than that obtained by multiplying the percentage of ferric oxide by 4.7165 and then subtracting 111.51%, or less than that obtained by multiplying the percentage of ferric oxide by 0.01407 and subtracting the result from 1.4560% and the percentage of other ceramic oxides not being greater than that obtained by multiplying the percentage of ferric oxide by 0.9859 and subtracting the latter result from 98.544%.

4. A resistor unit comprising an electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogeneous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 0 to 75% other ceramic oxides by weight, said other ceramic oxides being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the percentage of any heavy metal oxides other than said ferric oxide and said titanium dioxide not exceeding the percentage of said titanium dioxide, and in any said composition the percentage of titanium dioxide not being greater than that obtained by multiplying the percentage of ferric oxide by 4.7165 and then subtracting 111.51%, or less than that obtained by multiplying the percentage of ferric oxide by 0.01407 and subtracting the result from 1.4560% and the percentage of other ceramic oxides not being greater than that obtained by multiplying the percentage of ferric oxide by 0.9859 and subtracting the latter result from 98.544%, and metallic contact elements fused to said body at spaced positions thereon.

5. A resistor unit comprising an electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogeneous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 10 to 75% other ceramic oxides by weight, said other ceramic oxides being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the percentage of any heavy metal oxides other than said ferric oxide and said titanium dioxide not exceeding the percentage of said titanium dioxide, and in any said composition the percentage of titanium dioxide not being greater than that obtained by multiplying the percentage of ferric oxide by 4.7165 and then subtracting 111.51%, or less than that obtained by multiplying the percentage of ferric oxide by 0.01407 and subtracting the result from 1.4560% and the percentage of other ceramic oxides not

being greater than that obtained by multiplying the percentage of ferric oxide by 0.09859 and subtracting the latter result from 98.544%, and metallic contact elements fused to said body at spaced positions thereon.

6. A resistor unit comprising an electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogenous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 10 to 75% other ceramic oxides by weight, said other ceramic oxides including other heavy metal oxides and being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the percentage of said other heavy metal oxides not being greater than the percentage of said titanium dioxide, and in any said composition the percentage of titanium dioxide not being greater than that obtained by multiplying the percentage of ferric oxide by 4.7165 and then subtracting 111.51%, or less than that obtained by multiplying the percentage of ferric oxide by 0.01407 and subtracting the result from 1.4560% and the percentage of other ceramic oxides not being greater than that obtained by multiplying the percentage of ferric oxide by 0.9859 and subtracting the latter result from 98.544%, and metallic contact elements fused to said body at spaced positions thereon.

7. The method of producing a fired composition in the form of an electrically conducting ceramic body, which method comprises, forming a vitrifiable mixture of ceramic materials consisting of at least one titanium compound in an amount producing in the fired composition 0.05% to 63% titanium dioxide, at least one iron compound in an amount producing in the fired composition 23.88 to 99.95% ferric oxide, and other ceramic materials in an amount producing in the fired composition 0 to 75% of the corresponding oxides having a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the amount of any heavy metal compounds in said other ceramic materials producing a percentage of heavy metal oxides not greater than the percentage of titanium dioxide, the amount of titanium compound in any said mixture producing a percentage of titanium dioxide not greater than that obtained by multiplying the percentage of said ferric oxide by 4.7165 and then subtracting 111.51% and not less than that obtained by multiplying the percentage of said ferric oxide by 0.01407 and subtracting the result from 1.4560%, and the amount of other ceramic materials in any said mixture producing a percentage of said corresponding oxides not greater than that obtained by multiplying the percentage of said ferric oxide by 0.9859 and subtracting the latter result from 98.544%, all percentages being by weight of the ceramic composition after firing, and firing said mixture at a vitrifying temperature in an oxidizing atmosphere for sufficient time to produce a substantially homogeneous vitrified material in which the oxides have a state of oxidation equivalent to that of ferric oxide and titanium dioxide.

8. The method of producing a fired composition in the form of an electrically conducting ceramic body, which method comprises, forming a vitrifiable mixture of ceramic materials consisting of at least one titanium compound in an amount producing in the fired composition 0.05% to 63% titanium dioxide, at least one iron

compound in an amount producing in the fired composition 23.88 to 99.95% ferric oxide, and other ceramic materials in an amount producing in the fired composition 0 to 75% of the corresponding oxides having a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the amount of any heavy metal compounds in said other ceramic materials producing a percentage of heavy metal oxides not greater than the percentage of titanium dioxide, the amount of titanium compound in any said mixture producing a percentage of titanium dioxide not greater than that obtained by multiplying the percentage of said ferric oxide by 4.7165 and then subtracting 111.51% and not less than that obtained by multiplying the percentage of said ferric oxide by 0.01407 and subtracting the result from 1.4560%, and the amount of other ceramic materials in any said mixture producing a percentage of said corresponding oxides not greater than that obtained by multiplying the percentage of said ferric oxide by 0.9859 and subtracting the latter result from 98.544%, all percentages being by weight of the ceramic composition after firing, and firing said mixture at a vitrifying temperature in an oxidizing atmosphere for sufficient time to produce a substantially homogeneous vitrified material in which the oxides have a state of oxidation equivalent to that of ferric oxide and titanium dioxide.

9. A solid electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogeneous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 0 to 75% other ceramic oxides by weight, said other ceramic oxides being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the amount of any heavy metal oxides other than said ferric oxide and said titanium dioxide being not greater than the amount of said titanium dioxide, said composition having a specific resistivity of at least 1.5 ohms and not more than 30,000 ohms.

10. An electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogeneous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 10 to 75% other ceramic oxides by weight, said other ceramic oxides including other heavy metal oxides and being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the amount of said other heavy metal oxides being not greater than the amount of said titanium dioxide, said composition having a specific resistivity of at least 1.5 ohms and not more than 30,000 ohms.

11. A resistor unit comprising an electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogeneous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 0 to 75% other ceramic oxides by weight, said other ceramic oxides being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the amount of any heavy metal oxides other than said ferric oxide and said titanium dioxide being not greater than the amount of said titanium dioxide, said composition having a specific resistivity of at least 1.5 ohms and not more than 30,000 ohms, and metallic contact elements fused to said body at spaced positions thereon.

12. A resistor unit comprising an electrically conducting ceramic body having a negative temperature coefficient of resistance, said body being a fired substantially homogeneous vitrified composition consisting of from 0.05 to 63% titanium dioxide, 23.88 to 99.95% ferric oxide and 10 to 75% other ceramic oxides by weight, said other ceramic oxides including other heavy metal oxides and being in a state of oxidation equivalent to that of ferric oxide and titanium dioxide, the amount of said other heavy metal oxides being not greater than the amount of said titanium dioxide, said composition having a specific resistivity of at least 1.5 ohms and not more than 30,000 ohms, and metallic contact elements fused to said body at spaced positions thereon.

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