United States Patent

Brady

[15] **3,655,440**

[45] **Apr. 11, 1972**

[54] ELECTRICAL RESISTANCE ELEMENTS, THEIR COMPOSITION AND METHOD OF MANUFACTURE

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[22] Filed: **Mar. 3, 1969**

[21] Appl. No.: **803,688**

[52] **U.S. Cl.**.....**117/227,** 117/201, 106/1, 252/514, 338/308

[51] **Int. Cl.**.....**H01b 1/02,** H01b 1/08

[58] **Field of Search**.....117/227, 201; 106/1; 252/514; 338/308

[56] **References Cited**

UNITED STATES PATENTS

3,441,516	4/1969	Mulligan et al.	117/227 X
3,450,545	6/1969	Ballard et al.	106/1

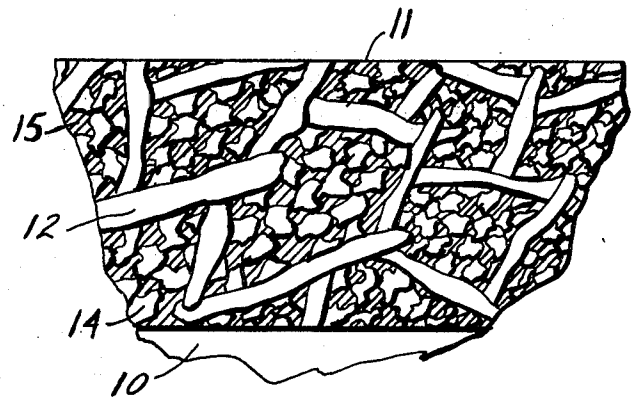
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[57] **ABSTRACT**

An electrically nonconductive crystal growth controlling agent comprising submicron inert particles is mixed with a crystalline conductive phase comprising an oxide of Ruthenium or Iridium, a vehicle, and a moisture impervious binder with which the inert particles will not react and in which the inert particles will not dissolve to any appreciable extent at elevated temperatures. After being applied to a high temperature-resistant, electrically nonconductive substrate, the composition is fired at elevated temperatures for a sufficient period of time to permit the crystals of the conductive phase to grow until an equilibrium condition is reached. This condition is determined in part by the crystal growth controlling agent. Upon cooling, the binder bonds together a composite mass comprising an inert intersticed matrix made up of the crystal growth controlling agent and the crystalline conductive phase which forms an interstitial mass within the interstices of the matrix. The method comprises the steps of thoroughly mixing the above-identified materials, applying a layer of the mixture to the substrate, and firing the substrate and layer of material for 45 to 60 minutes to a preferred peak temperature in the range of 975°–1025° C. During the firing cycle the crystals of the conductive phase increase in size until further growth is limited by the crystal growth controlling agent.

21 Claims, 3 Drawing Figures



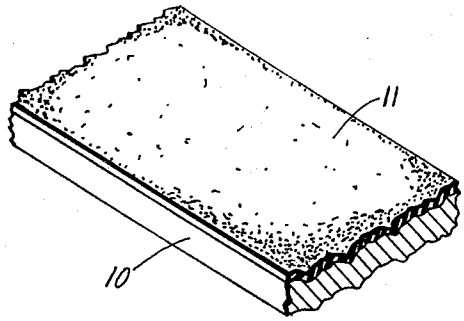


FIGURE-1

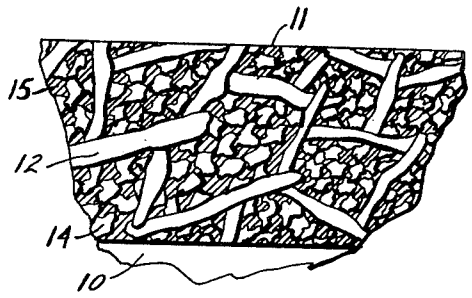


FIGURE-2

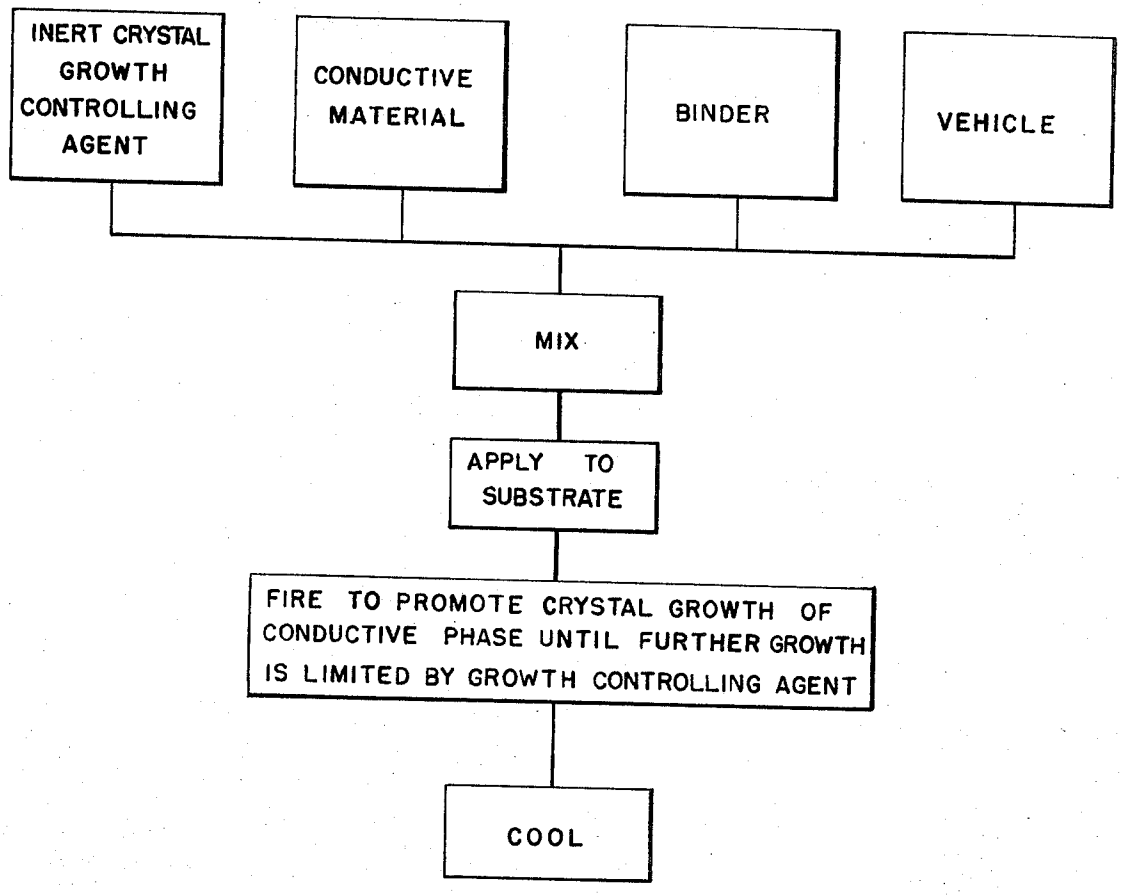


FIGURE-3

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ELECTRICAL RESISTANCE ELEMENTS, THEIR COMPOSITION AND METHOD OF MANUFACTURE

This invention relates to improved cermet resistance elements and to their composition and method of manufacture.

Cermet resistance elements and compositions known in the art are exemplified by U.S. Pat. No. 3,271,193 entitled "Electrical Resistance Element And Method Of Making The Same," issued to O. F. Boykin; and U.S. Pat. No. 3,304,199 entitled "Electrical Resistance element," issued to W. M. Faber, Sr., et al. Some of the heretofore known cermet resistance compositions and resistance elements made therefrom have exhibited characteristics suitable for many special applications. For example, in applications requiring exceptional thermal stability and low sheet resistances, resistance compositions such as those discussed in Boyd et al. U.S. Patent No. 3,372,058 have been very useful. However, general and widespread use of cermet compositions has still been limited because of objectionable amounts of electrical noise associated with resistance elements made from such materials and particularly so in the higher sheet resistance ranges currently attainable with such compositions. Usage of these compositions has also been limited because very high resistivity or sheet resistances have not been attainable therewith. Although the prior art discusses resistance materials having sheet resistances of up to about 500,000 ohms per square after firing, when these materials have been used to form the resistance elements in variable resistance controls the equivalent noise resistance of such controls has been of such great magnitude that it has far exceeded acceptable levels and in fact has not been measurable when following standard test procedures.

The prior art materials have not been usable in very high voltage applications as fixed or variable resistors because they have not had satisfactory voltage stability characteristics. More specifically, such materials have not been characterized by an acceptable sheet voltage coefficient of resistance when subjected to voltage gradients in excess of about 1,000 volts per linear inch of resistive path. Accordingly, it would be desirable to provide resistance elements and compositions that are stable at high voltages, i.e., that have a relatively low sheet voltage coefficient of resistance when subjected to high voltage gradients per inch of resistive path. As used herein, sheet voltage coefficient of resistance (Sheet VCR) means the number of parts change per million that one square of a resistive path exhibits when there is a change of 1 volt in the potential applied thereacross. Sheet voltage coefficient of resistance differs from the voltage coefficient of resistance (VCR) of a given resistance element in that the former quantity is not dependent on the geometry of the resistive path and can be readily used to compare one resistance element to another, whereas the latter quantity is a function of the geometry of the resistive path under consideration and can be meaningfully used for comparison only when the exact dimensions of the resistance element are specified. The sheet voltage coefficient of resistance and the voltage coefficient of resistance of a given resistance element are similar in that they both indicate essentially reversible or temporary changes due to changes in voltage. For example, if an increase of 1 volt will cause a given increase in resistivity, a decrease of 1 volt will cause a corresponding decrease. Thus, voltage coefficient of resistance and sheet voltage coefficient of resistance are not descriptive of the permanent change in resistive value that may occur during overload testing or "initial power stressing" as discussed for example in Kelly et al. U.S. Pat. No. 3,416,960 in connection with the problem of "power instability."

One type of electrical noise associated with cermet resistance elements is generated within the body of each element, is referred to as "current noise" in technical literature, and is measured as an increase in noise above the thermal noise of the element while current is being passed therethrough. This "current noise" is most often measured in decibels on Quan-Tech testing equipment of the type referred to in Kim U.S. Pat. No. 3,352,797 and manufactured by Quan-Tech Laboratories of Boonton, New Jersey; is normally referred to as "Quan-Tech" noise in the electronic components industry; and, to avoid confusion, will be referred to herein as Quan-Tech noise. Another type of electrical noise is encountered in variable resistance control application, is normally identified as "Equivalent Noise Resistance" (ENR), is associated with the movement of a contactor or wiper across the surface of a resistance element, and is measurable in ohms by following standardized test procedures as will be hereinafter more fully described. With the advent of solid-state devices such as transistors and integrated circuits, which are extremely "quiet" in comparison with vacuum tubes, it has become increasingly important to reduce the Quan-Tech noise levels in passive circuit elements such as cermet resistance elements in order to attain the reduced circuit noise levels that are possible when using such devices. It has also become increasingly important to reduce the ENR of variable resistance controls and particularly so when such controls include cermet resistance elements having relatively high sheet resistances.

Previously known resistance compositions have also had less than desirable voltage withstanding abilities. More specifically, the critical voltage gradient of resistors made from such compositions has been relatively low and when the applied voltage, per inch of resistive path, has been in excess of a critical level of about 800 volts, the prior art resistors have exhibited a drastic and permanent change in ohmic values. Since such resistors have been able to withstand only about 800 volts per inch of resistive path, it has been necessary to use extremely long resistive paths for high voltage applications. For example, such resistive paths would have to be at least 30 inches long in order to withstand a potential of 24,000 volts across the ends thereof. Accordingly, it would be desirable to provide improved resistance compositions and resistance elements having improved voltage withstanding abilities.

In addition to the problems and limitations of the prior art related to equivalent noise resistance, Quan-Tech noise, relatively low sheet resistances, voltage stability, and voltage withstanding abilities, another problem has long existed in connection with obtaining satisfactory production yields and particularly so when higher sheet resistances have been desired. Heretofore, relatively low production yields frequently have been accepted as unavoidable. In addition, in the case of many known cermet compositions having a sheet resistance in excess of 250,000 ohms per square, it has been necessary to sequentially deposit and fire two or more layers of such composition in order to obtain tolerable production yields. The problems of obtaining increased sheet resistances and acceptable production yields are considered at length in the aforementioned Daily et al. U.S. Pat. No. 3,329,526. Accordingly, it would be desirable to provide resistance elements and compositions therefore that are characterized by improved production yields, and by high sheet resistances.

Therefore, it is a general object of the present invention to provide an improved resistance element, composition, and method of making the same. Another object of the present invention is to provide an improved method of making a resistance composition and method of making an improved resistance element. A further object of the present invention is to provide an improved resistance element having an acceptable voltage coefficient of resistance per square when subjected to high voltage gradients. An additional object of the present invention is to provide an improved resistance element having a measurable low equivalent noise resistance. Yet another object of the invention is to provide an improved resistance element having a reduced Quan-Tech noise level. Yet a further object of the present invention is to provide cermet resistance elements having very high sheet resistances. Yet an additional object is to provide cermet resistance elements having a very high sheet resistance and comprised of a single fired layer of resistance composition. Still another object of the present invention is to provide a resistance element having an improved voltage withstanding ability. A still additional object of the

present invention is to provide improved compositions useful in making resistance elements that accomplish the above stated objects. A more specific object of the present invention is to provide compositions that provide improved production yields of electrical resistance elements. Another specific object of the present invention is to provide a cermet resistance composition wherein means are provided for controlling the growth of crystals of a conductive phase during a firing process. A still more specific object of the present invention is to provide a method of making a resistance element that includes the steps of firing a resistance composition and creating a molten glass environment for a crystalline conductive phase in the presence of means for controlling the growth of crystals of the conductive phase, and maintaining the composition at an elevated temperature until crystal growth is impeded by such means. Further objects and advantages of the present invention will become apparent as the following description proceeds, and the features of novelty characterizing the invention will be pointed out with particularity in the claims annexed to and forming a part of this specification.

Briefly, the present invention is concerned with improved resistance elements and with their composition and methods of manufacture. One specific composition embodying the invention comprises a crystal growth controlling agent in the form of electrically nonconductive, inert particles that are submicron in size. The composition further comprises a moisture impervious binder with which the inert particles will not react and in which the inert particles will not dissolve to any appreciable extent at elevated temperatures; a conductive phase; and a thermally decomposable or evaporable vehicle that facilitates the application of the resistance composition to a suitable substrate. In a specific embodiment of the invention, the composition includes a conductive phase comprising an oxide of ruthenium; a binder comprising glass particles; means for controlling the growth of the crystals of the oxide of ruthenium in the form of particles of alumina having an average particle size of 0.3 microns; and a conventional vehicle such as ethylcellulose. The composition is thoroughly mixed, applied to an alumina substrate by conventional silk screen methods, and fired to a peak temperature in the range of 975°–1025° C. in a 45 minute to 1 hour firing cycle. Firing the composition decomposes and drives off the organic ingredients and causes crystallographic changes to occur in the composition. The resistance elements are fired at elevated temperatures for extended periods of time so that the binder will become molten and the crystals of the conductive phase will increase in size until further increases are limited by the crystal growth controlling agent. After cooling, the crystal growth controlling agent forms an intersticed inert matrix, the conductive phase forms an interstitial mass within the interstices of the matrix, and the binder bonds together the matrix and conductive phase. Resistance elements embodying the present invention fulfill one or more of the above stated objects by exhibiting one or more of the following characteristics: a measurable low ENR of less than 1 percent in variable resistor applications; a very high sheet resistance; a Sheet VCR of 400 or less ppm per volt at voltage gradients of up to 3,000 volts per inch of resistive path; a surprisingly improved voltage withstanding ability; and consistently improved production yields.

For a better understanding of the present invention, reference may be had to the accompanying drawing wherein:

FIG. 1 is a fragmentary isometric view of an electrical resistance element embodying the present invention;

FIG. 2 is a very greatly enlarged cross-sectional view of a portion of the resistance element of FIG. 1 and is a two-dimensional representation of the microstructure of such resistance element; and

FIG. 3 is a flow chart illustrating the steps in the inventive method.

Recent research efforts have been directed to the development of a variable resistance control comprised of a cermet resistance element having a sheet resistance of 500,000 ohms or more per square. During the course of this work, it was discovered that the equivalent noise resistance between a movable contactor and the resistance element greatly exceeded acceptable limits when measured with a Model 400 X-Y recorder made by "Electro-Instruments" of San Diego, California. When using this recorder to measure the ENR of a resistor, standard procedures were followed by calibrating the equipment for the nominal overall ohmic value of the resistor to be tested and then continuously recording, as a percent of the overall ohmic value, the changes in resistance that occurred as the movable contactor was moved across the resistance element. By definition, such changes are the equivalent noise resistance of the resistor for each position of the contactor and are a measurement of the noise at the interface of the contactor and the resistance element. Following the above procedure, resistors normally are considered acceptable if the observed changes do no exceed 1 percent of the nominal overall ohmic value. When prior art type cermet resistance elements with a sheet resistance of about 500,000 ohms per square were treated, the observed ENR greatly exceeded 10 percent of the overall ohmic value of such elements.

I have found that the ENR of materials having a high sheet resistance can be reduced and maintained at acceptable levels by including a crystalline growth controlling agent, such as inert particles, in the resistance composition prior to firing. Somewhat surprisingly, the inclusion of such material in resistance compositions also provides resistance elements having improved voltage stability and voltage withstanding ability. The inert particles also may be used to provide resistance elements having significantly increased sheet resistances, i.e., in excess of 1 megohm per square, and, when such particles are included in prior art cermet resistance compositions, the production yield of such compositions can be significantly increased and significant reductions in Quan-Tech noise levels can be attained.

The aforementioned U.S. Pat. No. 3,304,199 teaches a preferred method of preparing cermet resistance compositions and elements. That preferred method comprises mixing a vitreous binder such as finely divided glass particles with a conductive material such as ruthenium dioxide or iridium dioxide and a liquid such as water or an organic vehicle to form a slurry. The liquid is then evaporated and the dry mixture of vitreous binder and conductive material is combined with a vehicle so that the resistive composition can be applied to a supporting substrate. The composition and substrate is then fired to fuse the vitreous binder to the surface of the substrate. Other patents, such as Place, Sr., et al. U.S. Patent No. 3,149,002 teach an alternative method of preparing cermet resistance compositions and elements wherein finely divided glass particles are mixed or milled with a resinate or other solution containing the constituents that will form the conductive phase of the resistor after firing. When resinates are used, the binder and resinate mixture is heated and stirred to remove the volatiles and organic materials from the mixture while decomposing the compounds in the resinate. After heating, the dry mixture is ground to a fine powder and calcined to assure removal of all organic materials. Thereafter the dry material is mixed with a suitable vehicle, applied to a desired substrate, and fired to fuse the mixture. According to the present invention, either of the aforementioned methods may be followed provided that the conductive material be capable of attaining a desired amount of crystal growth, that crystal growth controlling means be used to control such crystals growth, and that special firing procedures be followed, all as will be hereinafter more fully explained.

Although the exact reason for the significantly improved results obtained from the practice of the present invention are not fully understood, it is preferred that the crystal growth controlling means be very finely divided particles. Such particles must comprise a material with which the binder will not react at elevated temperatures. In addition, the inert particles must not dissolve to any appreciable extent in the binder at

elevated firing temperatures. As previously mentioned, the conductive phase must be capable of achieving crystal growth and, preferably, the conductive phase is a finely divided crystalline material, the crystals of which grow while being fired. The structural units of suitable crystalline material may be idiomorphic crystals, i.e., a group of space lattices of the same orientation that show symmetry by the development of regular faces, or allotrimorphic crystals that do not have regular faces. An allotrimorphic crystal is also referred to as an imperfect crystal, a xenomorphic crystal, or a grain. The term "crystal" is used generically herein to designate a crystalline structure, whether it be idiomorphic or allotrimorphic, since materials suitable for use in the present invention may be comprised of either one or both of these forms of crystals. During the firing step of the process the binder becomes molten and the crystals of the conductive phase increase in size in such molten environment until the inert particles control crystal growth by substantially impeding further crystal growth. After an equilibrium condition is approached, i.e., when the growth rate of the crystals has, for practical purposes, approached zero, the composition is cooled, and the inert particles form an intersticed matrix. The crystals of the conductive phase form an interstitial mass within the interstices of the matrix, and the binder bonds together the composite mass. The time required to approach the equilibrium condition depends of course on the firing temperature and on the nature of the materials being fired. Because of this, the firing conditions necessary to attain near equilibrium conditions for any given resistance composition can be most readily ascertained by firing each one of a plurality of substantially identical samples embodying the present invention at a selected high temperature for different periods of time and then graphically plotting the sheet resistance of each sample as a function of the corresponding firing time for each sample. When this is done, it will be observed that for an initial period of time the sheet resistance will vary as a function of time but that after such initial period, the sheet resistance will stabilize and very little additional changes in sheet resistance will be observable. Such stabilization of sheet resistance then indicates that an equilibrium condition has been approached. In addition, microscopic examination of the samples will reveal that the conductive crystals increase in size as the firing time is increased until an apparent maximum size is attained. The period of time required to attain such apparent maximum size corresponds quire closely to the initial period of time referred to above.

I have found that the withstanding voltage of the resistance element may be controlled by controlling the average particle size of the crystal growth controlling agent. Thus, if increased withstanding voltages and improved voltage stability are not desired, the crystal growth controlling agent may be formed of inert particles that have an average particle size as large as 20 microns. However, in order to obtain significantly improved withstanding voltages, i.e., withstanding voltages of about 3,000 volts or more per inch of resistive path, the inert particles are submicron in size and, preferably, have an average particle size of about 0.3 micron. If even higher withstanding voltages are desired, i.e., withstanding voltages in the neighborhood of 6,000 volts per inch of resistive path, the inert particles should have an average particle size of approximately 0.1 micron. The average particle size of the crystal growth controlling agent significantly affects the voltage stability and sheet resistance as well as the voltage withstanding ability of the fired resistance element. For example, when 0.3 micron particles are used, the Sheet VCR of the fired resistance material is 400 or less ppm per volt at voltage gradients of 3,000 volts per inch and higher and a sheet resistance of 600 megohms or higher per square may be obtained.

After compositions embodying the present invention have been applied by brushing, spraying, stenciling, transfer wheel, or screening onto the substrate, the composition is fired to a peak temperature sufficiently high for the binder to form a molten environment surrounding the crystals of the conductive phase and the crystal growth controlling agent. The peak firing temperature must be sufficiently high for growth of the crystals to occur at a reasonable rate. The maximum permissible peak temperature must be less than the volatilization temperature of the various portions of the resistance composition in the firing atmosphere and also less than the temperature at which either the conductive phase or crystal growth controlling agent become appreciably soluble in the binder or at which chemical reactions, pernicious to the desired characteristics of the fired resistance element, would take place between the various portions of the resistance composition or between such portions and the firing atmosphere. Each of the specific exemplifications mentioned herein were fired for 45 to 60 minutes in a conventional tunnel kiln to a peak temperature in the range of 975°–1025° C. Equally acceptable resistance elements were also obtained by firing the exemplary compositions for two to three hours to a peak temperature of 850° C. The former conditions are preferred because of the obviously reduced production or process time involved. Both of these firing conditions are more extensive than those used in the prior art.

As indicated by the flow chart of FIG. 3, the resistance composition is maintained at a sufficiently high temperature for a sufficient period of time to permit the crystals of the conductive material to grow or increase in size until the equilibrium condition is at least approximately attained. As this equilibrium condition is approached, the growth of the conductive phase crystals can be observed to diminish and apparently stop. As previously mentioned, the inert particles impede further crystal growth as the equilibrium condition is attained. Although the precise inter-action between the conductive crystals and inert particles is not precisely understood, I have found that when crystals of conductive material having an average size of about 1 micron are fired in the presence of 0.3 micron crystal growth controlling particles in a molten binder environment, the conductive crystals will grow to an equilibrium size of about 50 microns. In addition, even though it is difficult to determine the changes in final conductive crystal size that result from changing the size of the crystal growth controlling particles, it is possible to determine a preferred range of sizes of growth controlling particles that should be used to attain desirable electrical characteristics. For example, if crystal growth controlling particles having an average size greater than about 20 microns is used, significantly improved voltage stability and voltage withstanding ability characteristics will not be attained. On the other hand, if the crystal growth controlling particles used in the present exemplifications of the invention are colliodal in size, the fired resistance element is nonconductive.

The primary criteria for the specific inert material used as the crystal growth controlling means is the relationship between the inert material and binder. These materials must be selected so that the inert material will not chemically react with the vitreous binder (particularly during the firing cycle) and so that the inert material will not dissolve in the molten binder to any appreciable extent during the firing cycle. The problem of solubility is accentuated when the crystal growth controlling agent comprises particles in the micron and submicron size range because many materials that are relatively insoluble in a molten binder when the particle size is from 40 to 70 microns are objectionably soluble in the same molten binder when the particle size is in the micron and submicron range. As will be understood by persons skilled in the art, the determination of the relative solubility of two or more materials is best determined empirically, and "not soluble to an appreciable extent" is meant herein to refer to the observable characteristics of submicron alumina particles when subjected to a molten environment of lead-aluminia-silicate glass at from 850°–1,000° C. For the purpose of discussion herein, other materials will be considered to be not soluble to an appreciable extend in a given molten binder if the observable characteristics of micron and submicron particles in such binder are similar to the just mentioned characteristics of alumina.

With reference to the illustrated embodiment of FIG. 1, a substrate 10 formed of high alumina supports on a surface thereof a fired resistance element 11. FIG. 2 illustrates the characteristic microstructure of the resistance element 11 which comprises crystals 12 of a conductive phase, crystal growth controlling means in the form of inert submicron alumina particles 14, and a binder 15. It will be appreciated from an inspection of FIG. 2 that the particles 14 are not dissolved in the binder and that the particles 14 comprise an intersticed matrix, the crystals 12 form an interstitial mass within such matrix, and the binder 15 bonds the composite mass together. It will of course also be understood that FIG. 2 is a two-dimensional representation of a three-dimensional microstructure and that the conductive crystals 12 actually occupy random relative orientations and positions within the resistance element 11. The inert particles, selected conductive material, binder, and any well known vehicle are first thoroughly mixed together and then used to form an unfired resistance element. Although the unfired resistance elements could be of the volumetric type, in the exemplifications described hereinafter the unfired resistance elements were applied as a film to a substrate such as the substrate 10. The film and substrate were then fired so that the conductive phase crystals approached an equilibrium condition.

The constituents of two common glasses or vitreous binders that may be used as a moisture impervious binder in the practice of the present invention are as follows:

GLASS I

	Percent
PbO	65
SiO_2	34
Al_2O_3	1
Total:	100

GLASS II

	Percent
PbO	72.15
SiO_2	13.41
B_2O_3	9.04
ZnO	5.40
Total:	100.00

The following examples are exemplary cermet type resistance compositions formed in accord with the present invention. Some of the improved characteristics of fired resistance elements formed from such compositions are stated for each example and the percentage of composition is stated without regard to the presence of ethylcellulose or other well known vehicles since the amount of vehicle may be varied in manners well known in the art and depends primarily on the mode selected for depositing the resistance composition on the supporting substrate. In any case, the vehicle is decomposed and volatilized upon firing. Each of the resistance elements used to obtain the characteristics stated in the following examples was screened onto a high alumina substrate.

EXAMPLE A

	Percent by weight
Glass I	63.10
RuO_2	26.83
Al_2O_3 (0.3 micron average particle size)	10.07
	Total: 100.00

Sheet Resistance	405,200 ohms per square
Withstanding Voltage	3,000 volts per inch
Sheet VCR	400 or less ppm per volt

EXAMPLE B

	Percent by weight
Glass I	50.6
IrO_2	41.4
Al_2O_3 (0.3 micron average particle size)	8.0
	Total: 100.0

Sheet Resistance	600,000 ohms per square
Withstanding Voltage	3,000 volts per inch
Sheet VCR	400 or less ppm per volt

EXAMPLE C

	Percent by weight
Glass I	68.5
RuO_2	21.8
Al_2O_3 (0.3 micron average particle size)	9.7
	Total: 100.0

Sheet Resistance	20,000 ohms per square
Withstanding Voltage	3,000 volts per inch
Sheet VCR	400 or less ppm per volt

EXAMPLE D

	Percent by weight
Glass I	64.1
RuO_2	27.3
Al_2O_3 (7 micron average particle size)	8.6
	Total: 100.0

Sheet Resistance	100 ohms per square
Withstanding Voltage	(not meaningful for
Sheet VCR	(sheet resistances this low

EXAMPLE E

	Percent by weight
Glass II	67.5
RuO_2	23.1
Al_2O_3 (0.3 micron average particle size)	9.4
	Total: 100.0

Sheet Resistance	25,000 ohms per square
Withstanding Voltage	3,000 volts per inch
Sheet VCR	400 or less ppm per volt

EXAMPLE F

	Percent by weight
Glass I	70.1
RuO_2	19.9
Al_2O_3 (0.3 micron average particle size)	10.0
	Total: 100.0

Sheet Resistance	55,000,000 ohms per square
Withstanding Voltage	3,000 volts per inch
Sheet VCR	400 or less ppm per volt

EXAMPLE G

	Percent by weight
Glass I	74.2
RuO_2	15.3
$BaO.6Fe_2O_3$ (0.3 micron average particle size)	10.5
	Total: 100.0

Sheet Resistance	15,000 ohms per square
Withstanding Voltage	(Not meaningful for
Sheet VCR	(sheet resistances this low

EXAMPLE H

	Percent by weight
Glass I	71.0
IrO_2	18.8
Al_2O_3 (0.3 micron average particle size)	10.2
	Total: 100.0

Sheet Resistance	600,000,000 ohms per square
Withstanding Voltage	3,000 volts per inch
Sheet VCR	400 or less ppm per volt

Each of the above examples had an ENR of less than 1 percent of the nominal overall ohmic value of the resistance element. Resistance elements according to the present invention may comprise, on a weight basis, from 1½ to 30 percent of a crystal growth controlling agent and from 2 to 60 percent of conductive material. The preferred proportions of these materials are from 3 to 16 percent growth controlling agent and from 10 to 50 percent conductive material. By adjusting the proportions of the conductive material, binder, and growth controlling agent the sheet resistance of the fired resistance element can be controlled. The binder comprises the remainder of the resistance element and bonds together the fired matrix and conductive phase when the resistance ele-

ment is a film type element and also when the resistor is a volumetric type as disclosed for example in co-pending Holmes et al. application Ser. No. 506,449 filed on Oct. 24, 1965.

The crystalline conductive materials used in the examples above were in powdered form and had an average particle size, prior to firing, of 0.7 to 1 micron. For the most part, the particles comprised only a single crystal and thus the average crystal size was also 0.7 to 1 micron. The average particle size was determined with standard sub-sieve size measuring apparatus, whereas the average crystal size was determined with X-ray diffraction techniques. Using the same X-ray diffraction techniques, it was determined that after firing, crystals of the conductive phase had increased in size to between 40 and 80 microns and were about 50 microns, on the average. When control samples of cermet type resistance elements which did not include a crystal growth controlling agent were fired under the same conditions as Examples A–H above, the conductive crystals were several times larger in size than 50 microns and such elements, after firing, were no longer conductive.

The significantly improved production yields and Quan-Tech noise characteristics that may be obtained with the present invention will be appreciated from a comparison of the characteristics of the following Example I with the characteristics of Example A above. Example I typifies a prior art cermet composition and was fired in accordance with the prior art teachings for ten minutes in a tunnel kiln to a peak temperature of 830° C. It should be noted that the silicon dioxide used in Example I went into solution in the binder during the firing step and did not function as a crystal growth controlling agent.

EXAMPLE I

	Percent by weight
Glass II	95.00
RuO_2	1.67
SiO_2	3.33
	Total: 100.00

Sheet Resistance 399,100 ohms per square

When compositions according to Example I were applied as a single layer to form resistance elements, 65 percent of such elements had a sheet resistance of 399,100 ohms per square ±15.1 percent, and 95 percent of such elements had a sheet resistance of 399,100 ohms per square ±30.2 percent. The noise level of these elements was measured with a Quan-Tech Model No. 315 test set and observed to be +9 db. By comparison, when compositions embodying the present invention according to Example A above were applied to form single layer resistance elements, 65 percent of such elements had a sheet resistance of 405,200 ohms per square ±5.9 percent, and 95 percent of the resistance elements had a sheet resistance of 405,200 ohms per square ±11.8 percent. The Quan-Tech noise level of these elements was −17 db. From this comparison, it will be appreciated that the present invention results in production yield increases of more than 30 percent. In addition, Quan-Tech noise levels can be reduced by at least 26 decibels.

Various ones of Examples A through H above exhibit the greatly increased sheet resistances that are obtainable by practicing the present invention, and each of those examples also accomplish all of the stated objects of the invention. Although the above stated examples illustrate the use of RuO_2 and IrO_2 as the preferred materials to be used to form the conductive crystals in an inert matrix, it will be expressly understood that other crystalline materials may be used. The essential requirements of such materials are that they be electrically conductive and be capable of achieveing crystal growth in a molten binder environment. In addition, such crystal growth must be controllable by a crystal growth controlling means that is compatible, i.e., inert and substantially insoluble in the selected binder. Persons skilled in the art will understand that even though the oxidation state of all or part of the crystalline conductive phase may change during firing, the metallic constituents present in the resistance composition prior to firing are also present in the resistance element after firing. Thus, if a crystalline material such as elemental ruthenium or a ruthenium compound such as an oxide of ruthenium is present in the composition, ruthenium will also be a constituent of the crystalline conductive phase whether it appears in elemental form or in a compound, such as ruthenium dioxide.

A prior art cermet composition that uses palladium oxide-silver (PdO-Ag) as a conductive phase is sold commercially by E. I. DuPont de Nemours Co. as Resistive Formulation No. 7860. This formulation also includes a conventional vehicle and vitreous binder. Example J below consisted of 100 percent of the purchased formulation and was fired for 1 hour and 15 minutes to a peak temperature of 760° C. as specified by the manufacturer. Example K below was fired in the same manner (this provided a sound basis for comparison) and comprised 94 percent by weight of the above formulation No. 7860 and 6 percent by weight of 0.3 micron alumina.

EXAMPLE J

	Percent by weight
Formulation No. 7860	100

Sheet Resistance 75,000 ohms per square

EXAMPLE K

	Percent by weight
Formulation No. 7860	94
Al_2O_3 (0.3 micron average particle size)	6

Sheet Resistance 1,600,000 ohms per square

A comparison of Examples J and K reveals that the present invention clearly teaches how to attain one object of the invention, i.e., significantly greater sheet resistances than were heretofore contemplated, even though resistance elements according to Example K do not exhibit improved voltage stability or voltage withstanding ability. While the differences in characteristics exhibited by Example K and Examples A through H above are not fully understood, it is believed probable that various alloys are formed involving the non-oxidized noble metal constituent of Example K and that this alloying process interferes with crystal growth and crystal growth control. In addition, Example K compositions could not be fired at extremely high temperatures without becoming unstable, and this difference might also explain why improvements in stability, noise levels, and voltage withstanding abilities were not attained with such compositions.

Although alumina or barrium ferrite particles were used as the growth controlling agent in the above examples, substantially similar results can be obtained when other refractory materials are used. However, it must be emphasized that such other materials must satisfy the selection criteria set out hereinabove and can be neither colloidal in size nor have an average particle size in excess of about 20 microns. Steatite is one example of a material that is apparently too soluble in Glasses I and II to consistently yield the results obtainable in the above exemplary compositions. Although steatite was somewhat useful in compositions containing lesser relative amounts of binder, steatite was not useful on a substitute basis for the growth controlling agent in Examples A through H.

It will be appreciated by those skilled in the art that the materials used in the foregoing exemplifications were materials that are commercially available and that undoubtedly include unknown percentages of impurities. Also, production type equipment was used during processing and impurities may have been added to the exemplifications during such processing. In addition, other materials may be added by persons skilled in the art in order to attain special physical or electrical properties in addition to the desirable characteristics discussed herein. Accordingly, it will be understood

that resistance compositions and elements embodying the present invention may comprise such impurities and additives so long as they are not pernicious to the attainment of the stated objects of the invention.

From the foregoing, it will be seen that the present invention provides resistance elements having improved Quan-Tech and equivalent noise resistance characteristics, withstanding voltages and voltage stability, and greatly increased sheet resistances and production yields.

While there has been illustrated and described what are at present considered to be preferred embodiments of the present invention and a preferred method of making the same, it will be appreciated that numerous changes and modifications will occur to those skilled in the art, and it is intended in the appended claims to cover all those changes and modifications which fall within the spirit and scope of the present invention.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A resistance composition for making resistance elements having a resistance greater than 100 ohms and comprising by weight of solids, from 2 to 60 percent of a conductive material selected from the group consisting of Ru, Ir and their compounds, a glass vitreous binder, and from 1½ to 30 percent of inert noncolloidal chemically unreactive particles having an average particle size of less than 20 microns.

2. A resistance composition for making resistance elements having a resistance greater than 100 ohms and comprising a glass vitreous binder, at least 2 percent, by weight of solids of the composition, of conductive crystals selected from the group consisting of Ru compounds and Ir compounds that undergo crystalline growth and increase in size in a molten binder environment, and means for controlling the crystalline binder environment, and means for controlling the crystalline growth of the conductive crystals in a molten binder environment, said means comprising at least 1½ percent by weight of solids of the composition.

3. The composition of claim 2 wherein the conductive crystals comprise a compound selected from the group consisting of PdO, RuO_2 and IrO_2.

4. The composition of claim 2 wherein the means for controlling the growth of the conductive crystals comprises particles of inert noncolloidal chemically unreactive material having an average particle size of less than 10 microns.

5. The composition of claim 4 wherein the inert material comprises a refractory material selected from the group consisting of alumina and barium ferrite.

6. The composition of claim 4 wherein the particles of inert material comprise from 3 to 16 percent by weight of solids of said composition.

7. The composition of claim 6 wherein the conductive crystals comprise a compound selected from the group consisting of PdO, RuO_2 and IrO_2.

8. A resistance element having a resistance greater than 100 ohms and comprising an intersticed inert matrix, an interstitial mass of a conductive phase comprising conductive crystals selected from the group consisting of Ru compounds and Ir compounds disposed within said matrix, said matrix comprising inert noncolloidal chemically unreactive crystal growth controlling particles bounding the conductive crystals and spacing adjacent ones of said crystals, and a glass vitreous binder bonding together the composite mass.

9. The resistance element of claim 8 wherein the conductive phase comprises crystals having a size of from 40 to 80 microns.

10. The resistance element of claim 8 wherein the inert particles comprise from 1½ to 30 percent by weight of the element, and the conductive crystals comprise from 2 to 60 percent by weight of the element.

11. The resistance element of claim 8 wherein the crystal growth controlling particles have an average particle size of less than 20 microns.

12. The resistance element of claim 8 wherein the conductive crystals comprise a compound selected from the group consisting of PdO, RuO_2 and IrO_2.

13. The resistance element of claim 8 wherein the conductive crystals comprises a Pd compound.

14. The resistance element of claim 8 wherein the crystal growth controlling particles have an average particle size of from one-tenth micron to 10 microns and comprise from 3 to 16 percent, by weight, of the element, and wherein the conductive phase comprises crystals having a size of from 40 to 80 microns and comprises from 10 to 50 percent, by weight, of the element.

15. A resistance element having a resistance greater than 100 ohms and comprising an intersticed inert matrix, an interstitial mass of a conductive phase comprising conductive crystals comprising a compound selected from the group consisting of RuO_2, IrO_2, and PdO disposed within said matrix, said matrix comprising inert noncolloidal chemically unreactive crystal growth controlling particles comprising a refractory material selected from the group consisting of alumina and barium ferrite bounding the conductive crystal and spacing adjacent ones of said crystals, the crystal growth controlling particles having an average particle size of from one-tenth micron to 10 microns and comprising from 3 to 16 percent, by weight, of the element, and wherein the conductive phase comprises crystals having a size of from 40 to 80 microns and comprises from 10 to 50 percent, by weight, of the element, and a glass vitreous binder bonding together the composite mass.

16. A method of forming an electrical resistance element comprising the steps of: mixing together a binder, a conductive phase comprising crystals of a predetermined average size selected from the group consisting of Ru compounds and Ir compounds, particles of inert material having a predetermined average size, and a vehicle to provide a resistance composition, forming an unfired resistance element from the composition, firing the resistance element to a temperature of at least 760° C. to increase the size of crystals in the conductive phase, controlling the amount of size increase of said crystals in the conductive phase, and cooling the resistance element.

17. A method of forming an electrical resistance element comprising the steps of: mixing together a binder, a conductive phase comprising crystals of a predetermined average size selected from the group consisting of Ru compounds and Ir compounds, particles of inert material having a predetermined average size, and a vehicle to provide a resistance composition, forming an unfired resistance element from the composition, applying a layer of the composition to a high temperature resistant electrically nonconductive substrate, firing the resistance element for a period of time in excess of 45 minutes to a temperature of at least 760° C. to increase the size of crystals in the conductive phase, controlling the amount of size increase of said crystals in the conductive phase, and cooling the resistance element.

18. A method of forming an electrical resistance element comprising an intersticed matrix of inert particles, an interstitial mass of conductive crystals selected from the group consisting of Ru compounds and Ir compounds disposed within said matrix, and a binder bonding together the composite mass, said method comprising the steps of mixing together 2 to 60 parts by weight of conductive crystals that have a predeterminable average size and that increase in size in a molten binder environment, 1½ to 30 parts by weight of particles of an inert material, a moisture impervious binder, and a vehicle to provide a resistance composition, forming a portion of the composition into an unfired resistance element, liquefying the binder in said resistance element and promoting growth of conductive crystals in said resistance element, limiting the growth of said conductive crystals with the particles of inert material, and solidifying the binder to bond together the particles of inert material and conductive crystals.

19. A method of forming an electrical resistance element comprising an intersticed matrix of inert particles, an interst-

tial mass of conductive crystals disposed within said matrix, and a binder bonding together the composite mass, said method comprising the steps of mixing together 2 to 60 parts by weight of conductive crystals that have a predeterminable average size and that increase in size in a molten binder environment, 1½ to 30 parts by weight of particles of an inert material, a moisture impervious binder, and a vehicle to provide a resistance composition, forming a portion of the composition into an unfired resistance element, applying said portion to a high temperature resistance substrate, liquefying the binder in said resistance element by firing the resistance element for an extended period of time and at an elevated temperature and promoting growth of said conductive crystals in said resistance element, limiting the growth of said conductive crystals with the particles of inert material, and cooling the binder to bond together the particles of inert material and conductive crystals.

20. A method of forming an electrical resistance element comprising an intersticed matrix of inert particles, an interstitial mass of conductive crystals disposed within said matrix, and a binder bonding together the composite mass, said method comprising the steps of mixing together 2 to 60 parts by weight of conductive crystals that have a predeterminable average size and that increase in size in a molten binder environment, 1½ to 30 parts by weight of particles of an inert material, a moisture impervious binder, and a vehicle to provide a resistance composition, forming a portion of the composition into an unfired resistance element, applying said portion to a high temperature resistance substrate, liquefying the binder in said resistance element by firing the resistance element to a temperature of at least 975° C. and for at least 45 minutes promoting growth of conductive crystals in said resistance element, limiting the growth of said conductive crystals with the particles of inert material, and cooling the resistance element.

21. A method of making an electrical resistance element comprising conductive crystals, inert particles, and a binder and characterized by a high sheet resistance, a Sheet VCR of less than 400 parts per million per volt, and a voltage withstanding ability in excess of 1,000 volts per inch, said method comprising the steps of making a resistance composition by mixing together conductive crystals selected from the group consisting of Ru compounds and Ir compounds, inert particles and binder, forming an unfired resistance element from the composition, firing the resistance element to a temperature of at least 760° C. to provide a molten binder environment for the inert particles and conductive crystals in order to attain growth of the conductive crystals until an equilibrium condition is approached, and thereafter cooling the resistance element.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,655,440 Dated April 11, 1972

Inventor(s) Lynn J. Brady

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Specification:

Column 4, Line 21;	Change the word "treated" to ---tested---.
Column 6, Line 73;	Change the word "extend" to ---extent---.
Column 7, Line 31;	Delete the number "65" after the symbol "PbO"; under "Percent" insert -- 65 --.
Column 7, Line 33;	Delete the number "1" after the symbol "Al_2O_3"; under "Percent" insert -- 1 --.
Column 8, Line 9;	Change the number "20,000" to ---20,000,000---.

In the Claims:

Column 11, Line 35;	Delete the phrase "binder environment, and means for controlling the crystalline".

Signed and sealed this 7th day of November 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
☆ U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334

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