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ELECTRICAL RESISTANCE MATERIAL AND METHOD OF MAKING THE SAME

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3 Claims

ABSTRACT OF THE DISCLOSURE

An electrical resistance material and method of making the same wherein the material comprises a dispersion of large metal particles and small metal particles dispersed in a fused, glassy matrix, the sum of metal particles constituting about 25–80% of the material and the ratio of large to small metal particles being within the range of about 2:1 to 10:1.

This invention relates to the electrical resistor art, and more particularly to an electrical resistance material and method of making the same.

The present invention is particularly useful in the manufacture of potentiometers as well as variable and fixed resistors; however, it will be appreciated that the invention has broader applications, and may be used in the preparation of other types of electrical semi-conductors.

Resistors which may be prepared with the materials and methods of the present invention, are conventionally referred to as vitreous enamel-type resistors, or thick-film resistors. In general, these resistors comprise a non-conductive ceramic or glass support, and an electrically conductive film, of a thickness of at least about 50,000 Angstrom units thick, formed of a continuous phase or matrix of a fused glassy-type nonconductive material, containing a dispersion of electrically conductive particles. Heretofore electrically conductive material has taken the form of molecular metal, compounds containing ionic metal, and mixtures of these.

Many of the recent developments in this area of technology have been directed toward modifying the electroconductive ingredients in the resistor film, in an effort to improve the quality, reproducibility and range of resistance values obtainable.

For example, in accordance with one prior art practice, the electroconductive portion of the film is developed entirely from metal decomposed from an organo-metallic compound during fusion of the film. While resistors prepared from such films are useful for some purposes, they suffer two distinct disadvantages.

First, they tend to have poor dynamic noise properties (high contact resistance variations). This is a measure of the variation in resistance developed as a movable contact travels across the face of the resistor. Large variations make the material unsuitable for use in a potentiometer or variable resistor.

Second, such materials produce resistors over only a fairly narrow range of relatively high resistance values. This is true because there is a physical limitation as to the amount of organo-metallic compound which can be uniformly dispersed within the glassy matrix, and only a small portion of the organo-metallic compound is metal. Consequently, only about 16 wt. percent metal can be incorporated in a resistor produced in accordance with this method, and even with the maximum permissible amount of metal present in the composition, fairly high resistance values are developed.

In accordance with another prior art practice, the electroconductive portion of the film is developed from

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a mixture of metal particles and metal oxide particles. Here too, satisfactory resistors can be produced, however, in certain environments, the resistors, due to the presence of a metal oxide, tend to behave erratically and change resistance values. This is especially true in reducing atmospheres, where, apparently the metal oxide changes valence state and/or reverts to molecular metal.

It follows from the foregoing, that notwithstanding recent developments, there remains a need for improved resistor materials of the type described, which produce stable, reproducible electrical resistors, having a wide range of resistance values. The present invention is addressed to filling this need.

It has been found that the above desiderata can be realized by producing the electroconductive portion of the electrical resistance material, entirely from molecular, i.e., elemental metal of two distinctly different particle sizes. The larger metal particles may have a size within the range of about .01 to about 100 microns with most of the particles being in the range of about 1 to about 50 microns, and can be derived by subdividing massive metal in accordance with techniques described more fully hereinafter. The smaller metal particles are essentially of molecular size, and are derived by the in situ decomposition of an organo-metallic compound, such as, for example a metal resinates. Resinates are preferred because of their availability, however it is to be understood that other organic compound complexes of the metals listed hereinafter may be used so long as they decompose to release molecular metal during the firing of the resistance material.

The total metal content of the electrical resistance material should fall within the range of about 25 to about 80% by weight, and the ratio of large to small metal particles should be within the range of about 2:1 to about 10:1. Further, both sizes of metal particles should be selected from the group consisting of gold, silver, platinum, rhodium, iridium, alloys and mixtures thereof.

By way of example only, and without intending to limit the scope of the invention, practice of the present invention has produced satisfactory resistors having resistance values over the range of 16 to about 160,000 ohms per square.

Since only a portion of the total metal value of the resistance material is derived from the decomposition of organometallic compounds, resistors having much higher conductivities are obtainable than is the case in prior art practices where the total metal value is derived from the decomposition of organo-metallic compounds.

Further, since essentially all of the electroconductive portion of the resistance material is in the form of molecular, i.e., elemental metal, resistors produced therefrom are far more stable, even in reducing environments, than is the case of resistors containing electroconductive metal oxides or other ionic forms of metal.

Still further, it has been found that resistors produced in accordance with the present invention have improved dynamic noise characteristics (lower contact resistance variations) than is the case of resistors produced in accordance with the prior art. The reason for this is not fully understood but the improvement may be attributable to the presence of higher metal concentrations at the surface of resistance materials produced in accordance with the practices of the present invention.

Another aspect of the present invention is concerned with an improved method of preparing electrical resistance materials. This comprises admixing a finely divided glassy material, metal particles, and at least one heat decomposable organo-metallic compound in the presence of a sufficient quantity of liquid vehicle to form a paste;

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applying the paste to a support; and heating the supported paste at an elevated temperature, to drive off the vehicle, decompose the organo-metallic compound, and fuse the glassy material. It is important that the decomposition of the organo-metallic compound, and fusion of the glassy matrix take place in situ after the composition is applied to a suitable support. It has been found that if the composition is fused, and fritted, prior to application to a support, and then re-fused to support, that a satisfactory resistor will not be produced.

It is therefore an object of the present invention to provide an improved electrical resistance material.

A further object of the invention is to provide an electrical resistance material having improved electrical properties over a wide range of resistor values.

Still another object of the invention is to provide an improved resistance material containing large and small metal particles, in which the ratio of large to small particles is within the range of about 2:1 to about 10:1.

Yet another object of the invention is an improved method for making electrical resistors having improved electrical properties.

The following materials were used in the examples described below:

| Resinate A | | |
|-------------|-------|-------------|
| Ingredient: | | Wt. percent |
| Gold | ----- | 3.92 |
| Iridium | ----- | .98 |
| Platinum | ----- | .20 |
| Base oxides | ----- | 1.00 |
| Organic | ----- | 93.90 |

Commercially available as Squeegee Bright Platinum 7278.

| Resinate B | | |
|-------------|-------|-------------|
| Ingredient: | | Wt. percent |
| Gold | ----- | 15.00 |
| Platinum | ----- | 2.00 |
| Rhodium | ----- | .07 |
| Base oxides | ----- | .30 |
| Organic | ----- | 82.63 |

Commercially available as Squeegee Bright Platinum 775.

| Alloy A | | |
|--------------|-------|-------------|
| Ingredient: | | Wt. percent |
| Gold | ----- | 55.0 |
| Platinum | ----- | 15.0 |
| Other solids | ----- | 15.0 |

Commercially available as Squeegee Gold Alloy Paste A-1199.

| Alloy B (-325 mesh) | | |
|---------------------|-------|-------------|
| Ingredient: | | Wt. percent |
| Gold | ----- | 66.6 |
| Silver | ----- | 33.4 |

Glaze A

Glass (commercially available lead borosilicate-based glass in frit form).

Organic Vehicle (Squeegee medium 6633).

Glaze B

Same as Glaze A but diluted with organic vehicle (Squeegee medium 6633) to provide a 30% solids concentration.

Commercially available as Squeegee over Gold Glaze 6624.

Alloy B was prepared in the following manner:

The gold and silver raw materials were weighed in the proportion indicated above, mixed and melted at about 1100° C.

On cooling, a "button" of alloy was formed which was then rolled into a thin sheet which in turn was cut into chips measuring about 1/4 inch square.

The chips were gross pulverized by passing them repeatedly through a hammer mill provided with progres-

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sively finer screens until a +325 product was obtained.

Thereafter the mill was provided with a recirculation system whereby a water slurry of alloy particles was recycled through the mill until essentially all of the solids passed through a 325 mesh screen into an accumulation.

The -325 particles were separated from the water by centrifugation and decantation, and then dried.

EXAMPLE I

A composition was prepared by thoroughly admixing the following ingredients in the proportions indicated:

| Ingredients: | Parts by wt. |
|--------------|--------------|
| Resinate A | 2.50 |
| Resinate B | 0.55 |
| Alloy A | 1.00 |
| Glaze A | 1.50 |

The composition was deposited on a ceramic support (to which terminals had been fired previously) by screening through a 400 mesh graining-type screen.

The supported composition was then heated gradually in a kiln to a firing temperature within the range of about 550° C. to about 565° C., maintained in the firing range for not more than about 10 minutes, and then gradually cooled. The entire thermal cycle spanned about an hour's time.

The fired resistance material had the following compositions:

| Ingredient: | Wt. percent |
|-----------------------|-------------|
| Metal from resinsates | 15.5 |
| Metal from alloy | 36.8 |
| Glass | 47.7 |

It will be seen from the foregoing that the total metal content was 52.3% and the ratio of larger metal particles (from the alloy) to smaller metal particles (from the resinsates) was slightly more than 2:1.

This material had a resistance of 278 ohms per square.

EXAMPLE II

The procedure described in Example I was repeated except that the composition was modified by the inclusion of an additional 3 parts of Glaze A.

Thus the compositions used contained the following ingredients in the proportions indicated:

| Ingredient: | Parts by wt. |
|-------------|--------------|
| Resinate A | 2.50 |
| Resinate B | 0.55 |
| Alloy A | 1.00 |
| Glaze A | 4.50 |

It will be seen that the glaze in the above composition constituted about 53% by weight of total composition as compared to about 27% by weight for the composition used in Example I.

The fired film produced a very satisfactory resistance material having the following composition:

| Ingredient: | Wt. percent |
|-----------------------|-------------|
| Metal from resinsates | 7.85 |
| Metal from alloy | 18.90 |
| Glass | 73.25 |

The ratio of large to small metal particles remained at slightly better than 2:1, but the doubling of the glass content reduced the total metal content to 26.75%.

This material had a resistance of 167,000 ohms per square.

EXAMPLE III

A composition was prepared by thoroughly admixing the following ingredients in the proportions indicated:

| Ingredient: | Parts by wt. |
|---------------------|--------------|
| Resinate A | 3.69 |
| Resinate B | 1.35 |
| Alloy B (-325 mesh) | 4.50 |
| Glaze B | 3.78 |

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The composition was deposited on a ceramic support (to which terminals had been fired previously) by screening through a 325 mesh graining-type screen.

The supported composition was then heated gradually in a kiln to a firing temperature within the range of about 572–580° C., maintained in this range for not more than about 10 minutes, and then gradually cooled. The entire thermal cycle spanned about an hour's time.

| Ingredient: | Wt. percent |
|-----------------------------|-------------|
| Metal from resinsates ----- | 7.2 |
| Metal from alloy ----- | 73.5 |
| Glass ----- | 19.3 |

Here the total metal content was 80.7% and the ratio of large to small metal particles, slightly more than 10:1.

The fired material had a resistance of 16.7 ohms per square.

EXAMPLE IV

The procedure described in Example III was repeated except that the composition was modified by the inclusion of an additional 7.78 parts of Glaze B.

Thus the composition used contained the following ingredients in the proportions indicated:

| Ingredient: | Parts by wt. |
|---------------------------|--------------|
| Resinate A ----- | 3.69 |
| Resinate B ----- | 1.35 |
| Alloy B (—325 mesh) ----- | 4.50 |
| Glaze B ----- | 11.56 |

It will be seen that the glaze in the above composition constituted about 55% by weight of total composition as compared to about 28% by weight for the composition used in Example III.

The fired film produced a very satisfactory resistance material having the following composition:

| Ingredient: | Wt. percent |
|-----------------------------|-------------|
| Metal from resinsates ----- | 5.22 |
| Metal from alloy ----- | 53.20 |
| Glass ----- | 41.58 |

The ratio of large to small metal particles remained at slightly better than 10:1, but increasing the glass content reduced the total metal content to less than 60 wt. percent.

This material had a resistance of 1,390 ohms per square.

As previously noted it is important in the practice of the method of the present invention that the decomposition of the organo-metallic compound and fusion of the glassy matrix take place in situ after the composition is applied to a suitable support. Failure to follow this procedure will not produce a satisfactory resistance material. This was established by a number of experiments, of which the following is exemplary.

EXAMPLE V

The following ingredients were weighed into a fused quartz crucible and then mixed on a three roll paint mill:

| Ingredient: | Grams |
|--|-------|
| PbO ----- | 27.0 |
| B ₂ O ₃ ----- | 2.0 |
| SiO ₂ ("Potters Flint") ----- | 6.0 |
| Gold resinate (24% Au) ----- | 48.5 |

The composition was then slowly heated in a kiln to 700° C.; allowed to cool; reheated to 1200° C.; and while molten, poured in to water to form a frit.

The frit was milled in a ball mill for 72 hours and then screened through a 325 mesh sieve screen.

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The treated frit was incorporated in the following composition:

| Ingredient: | Wt. percent |
|-----------------------------------|-------------|
| Treated frit ----- | 2.0 |
| Platinum powder (—325 mesh) ----- | 2.0 |
| Silk screen medium ----- | 1.5 |

The composition was mixed and milled on a three roll paint mill and then deposited on suitable ceramic supports through a 325 mesh graining type screen.

Various specimens were then fired in a kiln to 570° C., 620° C., and 670° C.

The resistance material on each specimen was found to have infinite resistance, indicating that none were satisfactory resistors.

It is believed that this result is due at least in part to the observed phenomenon of a phase separation of metallic gold decomposed from resinate, prior to fritting. Apparently even subsequent redispersion of the gold through milling was incapable of providing the film with an electroconductive property. This points up the importance of decomposing the organo-metallic compound in situ to ensure uniform dispersion of small metal particles.

EXAMPLE VI

The improved stability of resistance elements prepared in accordance with the present invention was established in the following manner:

A series of resistance elements having resistance values varying from about 27,000 ohms to about 2 megohms were prepared in accordance with the procedures described in Examples I and II.

A second series of resistance elements were prepared from commercially available materials (Du Pont's Palladium-Silver #8020 and #8025) in accordance with the manufacturer's specifications. These materials are believed to contain palladium oxide and metallic silver. They were processed into resistance elements having resistance values ranging from about 15,000 ohms to 2 megohms.

Specimens from both series were placed in a container which in turn was placed in an oven the container was closed except for gas inlet and outlet openings.

With the oven preset at a temperature of 150° C., the container was continuously purged with a preheated reducing atmosphere consisting of "forming gas" (85% N₂ and 15% H₂) for 30 minutes.

Resistance readings were taken before and after exposure to the forming gas, with the following results:

COMMERCIAL RESISTORS

| | Initial resistance (ohms) | Resistance after exposure (ohms) | ΔR | Percent ΔR |
|----|---------------------------|----------------------------------|--------|------------|
| 55 | 15,030 | 10,640 | -4,390 | -29 |
| | 14,160 | 12,380 | -1,780 | -12.5 |
| | 14,070 | 10,630 | -3,440 | -24 |
| | 12,360 | 9,518 | -2,842 | -23 |
| | 1,905,000 | 1,910,000 | +5,000 | +0.26 |
| | 2,004,000 | 2,010,000 | +6,000 | +0.30 |
| | 27,170 | 27,170 | 0 | 0 |
| | 27,970 | 27,970 | 0 | 0 |
| 60 | 31,920 | 31,920 | 0 | 0 |
| | 1,551,000 | 1,551,000 | 0 | 0 |
| | 1,414,000 | 1,414,000 | 0 | 0 |
| | 1,940,000 | 1,940,000 | 0 | 0 |

These data show that resistors prepared in accordance with the present invention are far more stable to exposure to a reducing atmosphere than are resistors prepared from commercial materials.

The present invention has been described in conjunction with certain specific embodiments; it will be appreciated that these were described for illustrative purposes and that many modifications will readily suggest themselves to those skilled in the art.

Having thus described my invention, I claim:

1. An electrical resistance material comprising a dispersion of large metal particles of a size within the range

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of about 0.01 to about 100 microns and small metal particles of essentially molecular size in a fused, glassy matrix, the sum of metal particles constituting from about 25 to about 80% by weight of the resistance material, the ratio of large to small metal particles being within the range of about 2:1 to 10:1, and both sizes of particles being formed of a metal selected from the group consisting of gold, silver, platinum, rhodium, iridium, alloys and mixtures thereof.

2. The electrical resistance material as defined in claim 1 wherein said fused glassy matrix comprises a borosilicate glass.

3. The electrical resistance material as defined in claim 2 wherein said borosilicate glass is modified with a com-

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pound selected from the group consisting of lead oxide and the alkaline earth metal oxides.

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DOUGLAS J. DRUMMOND, Primary Examiner