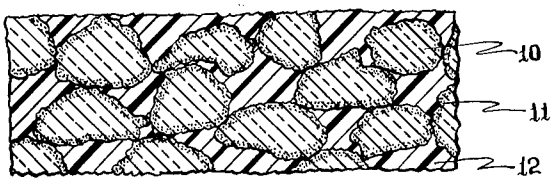
Sept. 13, 1955 D. B. PECK 2,717,946

ELECTRICAL RESISTANCE ELEMENTS

Filed Oct. 14, 1950

FIG. 1



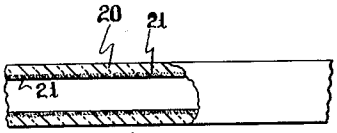




FIG. 2A

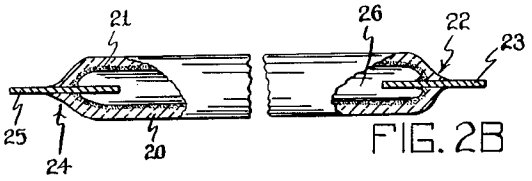



FIG. 2B

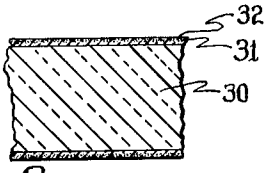



FIG. 3

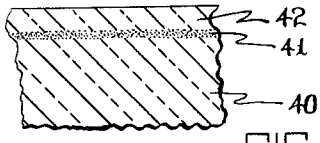



FIG. 4

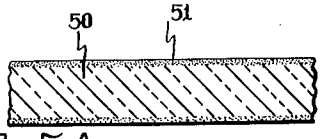



FIG. 5A

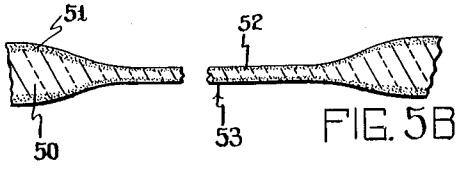



FIG. 5B

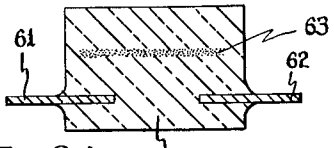



FIG. 6A

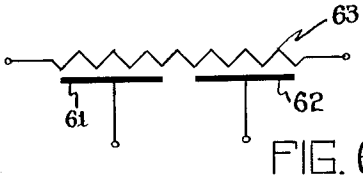



FIG. 6B

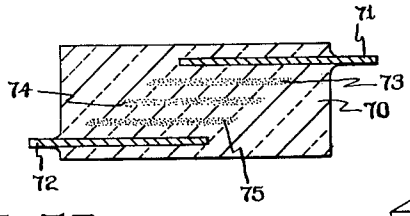



FIG. 7B

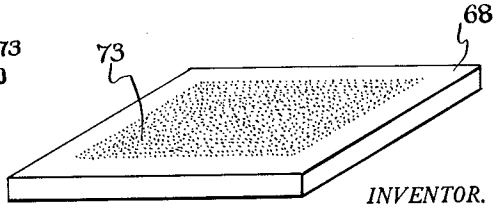



FIG. 7A

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# ELECTRICAL RESISTANCE ELEMENTS

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Application October 14, 1950, Serial No. 190,109

6 Claims. (Cl. 201—73)

This invention relates to improved electrical elements and more particularly refers to novel electrical resistors.

Precision resistors have in the past been made principally by two processes. First, metal and metal alloy wire wound resistors have been employed, particularly in the low resistance, high power values. Second, vitreous carbon has been deposited upon porcelain, steatite and similar ceramic base elements. The former are characterized by good stability and by low temperature and voltage coefficients of resistance. However, they are relatively expensive, particularly when high resistance values, say above 1 megohm, are required, because of the length and size of wire required. Further, they are large and bulky for such high resistance values, particularly in view of the low wattage normally encountered in the high resistance applications.

Vitreous carbon resistors are cheaper and can be made in fairly close resistance tolerances by spiral cutting of the deposit, etc. However, the temperature and voltage coefficients of resistance are inferior, particularly in resistance values in excess of $10^9$ ohms.

Numerous other processes have been proposed to overcome the above disadvantages and produce a stable, inexpensive, high resistance value unit. Metallized glass, carbon suspensions in gelatin or resin and similar modifications have been investigated. However, none of these appear to meet the stringent specifications for high stability, high resistance ($10^9$—$10^{15}$ ohms) service.

It is an object of the present invention to overcome the foregoing and related disadvantages. A further object is to produce new and improved resistance elements. A still further object is to produce insulated resistance elements of exceptional electrical stability and physical durability. Additional objects will become apparent from the following description and claims.

In this description:

Fig. 1 is a fragmentary sectional view of one embodiment of the present invention;

Figs. 2A and 2B are partly broken away views showing other embodiments of the present invention;

Figs. 3, 4 and 5A are fragmentary views similar to Fig. 1 of still further embodiments of the present invention;

Fig. 5B shows a modified form of the embodiment of Fig. 5A;

Fig. 6A is a sectional view of yet another embodiment of the present invention;

Fig. 6B is a schematic diagram showing an equivalent electrical circuit provided by the construction of Fig. 6A;

Fig. 7A is an isometric view of a construction element in accordance with the present invention; and

Fig. 7B is a sectional view similar to Fig. 6A of a further construction embodying the present invention made from elements of the type shown in Fig. 7A.

The invention is generally concerned with a process for producing electrical resistance elements which comprises subjecting solid solution of inorganic oxides containing from about 3% to about 82% of oxides of metals selected from the class containing the metals of



the B sub-groups of groups I, IV and V in the fourth and sixth periods of the periodic table to a reducing atmosphere at a temperature between about 75° and about 600° C. This process is made the subject of a number of improvements which lead to production of new and useful resistance elements.

The reducibility of glasses containing lead oxide, bismuth oxide and antimony oxide and silver oxide, for example has been known for many years; likewise, the surface conductivity of the glasses made up with one or more of the above oxides and subsequently reduced has been noted. Unfortunately, however, the characteristics of the known reduced glass, as a resistance element, are not entirely satisfactory, and inferior for hi-megohm applications. The present invention substantially overcomes the difficulties of the prior art. For example, one defect has been the marked negative temperature coefficient of resistance of the resistors. Another has been the instability of the resistor as a function of time; resistors show an appreciable and progressive increase in resistance value with time.

According to one embodiment of the invention, the glass composition is finely ground prior to reduction, to produce small particles, the surfaces of which are then reduced by heating in a reducing atmosphere. The resulting powder may be incorporated in a glass melt, to produce a solid massive resistance element not heretofore attainable. The powder may optionally be suspended in a resinous or other insulating binder to produce a resistance ink or lacquer having characteristics superior to carbon and graphite inks, particularly for high resistance values where carbon and graphite resistors are unsatisfactory.

This embodiment is illustrated in Figure 1 which shows a number of glass particles **10**, the surfaces of which are reduced to provide a conducting colloidal suspension **11** of metal particles within the matrix and on the surface of glass **10**. The reduction is accomplished on loose powder and subsequently the particles may be joined together with a binder such as indicated at **12** as a resin, by incorporation in a glass melt or actually by fusion of adjacent particles together by heating, preferably in a reducing atmosphere, above the softening point of the glass.

According to another embodiment of my invention, the resistant element may be produced and provided with a hermetic housing by a simple and inexpensive process. A tubular element of the reducible glass is treated by passing a reducing gas through the bore of the tube under suitable temperature conditions, reducing the inside surface only of the glass tube. Thereafter, terminal wires are inserted in short lengths of the tubing and sealed thereto, usually with an inert gas within the freeboard.

Figures 2A and 2B illustrate this embodiment. Tube **20** fabricated from a glass composition suitable for reduction is placed in a furnace and reducing gas passed through the center of the tube. The inside surface of tube **20** thus is provided with a resistance coating **21**. Alternately, the tube may be treated with very hot reducing gas. Figure 2B shows the tube of Figure 2A processed to produce a finished resistor. The tube **20** is fused at the ends **22** and **24** to terminal wires **23** and **25** respectively. The free board within the sealed housing is preferably filled with an inert gas such as nitrogen. Resistance layer **21** contacts terminal wires **23** and **25** at the point of fusion.

According to another embodiment of my invention, I produce a resistance element with unusually low temperature coefficient of resistance by providing an inorganic insulating base with a linear temperature coefficient of expansion of less than about $1.0\times10^{-6}$/° C. On this

base there is fused a layer of reducible glass possessing a thickness of less than about 0.01", whereby the expansion of the reducible glass layer is determined by the underlying base. Subsequently, the surface of the glass overlay may be reduced as elsewhere described.

In Figure 3 is shown an inorganic insulating base **30** possessing a linear temperature coefficient of expansion of less than $1.0 \times 10^{-6}$/° C. On the surface of this is fused a layer of reducible glass **31** in a thickness less than .01" and preferably less than about .002". The surface of this overlayer is reduced by reduction to form a conducting film 32. The temperature coefficient of resistance of the resistor thus produced will be extremely low. Suitable materials include special silica glass, quartz and steatites. Some of the latter are particularly desirable, possessing very, very low temperature coefficients.

According to yet another embodiment of my invention, I improve the stability of the reduced glass resistors by an oxidation of the surface of the glass, following the reduction treatment. As a result the surface layer is not appreciably sensitive to air and oxidizing atmospheres over the temperature range normally met in resistor operation.

This is shown in Figure 4 in which a reducible glass mass **40** is treated at appropriate temperatures in a reducing atmosphere to produce a surface layer of colloidal metal particles **41**. After this process, the mass is subjected to heat treatment for a limited time in an oxygen atmosphere or other oxidizing atmosphere to produce an insulating surface layer **42** above the conducting layer **41**. Ordinarily, this process of reoxidation is conducted for about 10 minutes at a temperature corresponding to the reduction temperature.

In accordance with another embodiment of my invention, I control the resistance values obtainable from any given glass composition, reduced under a particular set of conditions, by heating the glass member to its softening point and stretching the glass until the resistance has increased to the desired value per square or other measuring unit. This is applicable with plates, tubes, rods, etc.

Figure 5A shows a glass rod **50**, the surface of which has been reduced to provide resistance layer **51**, as elsewhere described. Figure 5B shows the rod after it has been heated preferably in a reducing gas flame above its softening point and drawn to a smaller diameter and accordingly a higher resistance value per square or per unit length. **53** is the glass element with reduced diameter containing thin resistance surface layer **53**. It is to be understood that the converse process may be applied, e. g., the mass may be heated above its softening point and then compressed to increase the concentration of metal particles in any given surface layer.

Another embodiment of my invention is concerned with the production of resistance layers within glass laminates, for use as circuit elements in filters, networks and other multiple assemblies, or for use as voltage stress equalizing "floating" foils in high voltage and high frequency capacitors, to reduce or eliminate corona effects and increase breakdown voltage.

Figure 6A shows a simplified cross section of a fused glass filter circuit in which solid metal electrodes **61** and **62** are embedded in glass mass **60**. Conducting layer **63** serves as a capacitor electrode as well as a partially distributed resistance element. Such an element would be constructed by stacking or rolling of several films of reducible glass, one of which has been reduced to provide conducting layer **63**. After the stacking or rolling, the assembly is heated above the melting point of the glass to fuse the assembly together. Figure 6B shows a schematic representation of the circuit produced. Capacitor elements **61** and **62** face against and are distributed along resistance element **63**.

Figures 7A and 7B show a further and extremely advantageous construction of the invention. The capacitor is wound or stacked with at least one resistance layer on a thin glass plate which is fused into the capacitor assembly. Figure 7A shows a plate **68**, a portion of one surface of which is exposed to a reducing atmosphere at high temperatures to produce conducting layer **73**. One or more of such layers is stacked with unreduced layers and capacitor electrodes to produce after fusion a structure such as that shown in Figure 7B. For example, electrodes **71** and **72** are separated by a glass mass **70** in which are fused staggered floating electrodes **73**, **74**, and **75**. These electrodes serve to increase the corona starting voltage and raise the breakdown voltage of the capacitor without appreciable effect upon the series resistance of the capacitor. Because layers **73**, **74** and **75** are extremely thin, their effect is merely to distribute the energy field uniformly between terminal electrodes. It is to be understood that portions of the capacitor assembly may be made up with glass sheets which do not reduce under the conditions of treatment but which do fuse in the temperature range of the reducible glass constituents. It is well known, however, that lead silicate glasses are characterized by unusually desirable dielectric properties if reduction be avoided.

The reducible elements referred to herein are ordinarily selected from the class initially containing from about 3% to about 82% of lead oxide, silver oxide, gold oxide, antimony oxide, bismuth oxide or tin oxide. Preferred oxides are bismuth oxide and lead oxide. For a number of reasons, lead oxide is a particularly desirable oxide for use in accordance with the present invention. Mixtures of these oxides are also useful.

Other constituents of the solid solutions ordinarily consist of sodium and/or potassium oxides, slica, calcium oxide, lithium oxide, beryllium oxide, magnesium oxide, aluminum oxide, iron oxide, zinc oxide, etc. These materials and the oxides previously specified may occur in combined form with silica or boron oxide, e. g. sodium silicate, lead silicate, lead borate, etc. Further, fluorides and other materials may be employed as fluxing and modifying agents. It is preferable to avoid the presence of aluminum oxide and appreciable quantities of boron oxide.

The expression "solid solution" is intended to mean the hard, solid state, in which some non-crystalline phases are present. However, it need not be a transparent glass and, in some cases, will be a translucent or opaque vitreous material, as for example, an enamel. Potassium lead silicate enamels are representative of the latter.

The reduction treatment described herein appears to reduce certain oxides to the inactive metal state, in what appears to be colloidal particles suspended in the glass.

The amount of reduction is controlled by a number of factors, e. g. temperature, material composition, time, gas pressure, boiling point of the reduced metal, gas diffusion rates, etc.

The reducing atmosphere may consist of hydrogen, methane, illuminating gas, etc. While the pressure employed is normally atmospheric, it may be reduced or increased if so desired. The time is usually between about 5 minutes and about 24 hours, depending upon the resistance value desired, the temperature and other factors.

According to my preferred practice, the temperature of reduction is such that the vapor pressure of the metal reduced does not exceed 0.0001 mm. Hg. The temperature of initial oxide reduction is an important variable in the process. The usual range of temperature is from about 75° C. to about 600° C. while the preferred range for most materials is from about 100° C. to about 400° C. The solid solutions containing lead oxide may be treated with excellent results at a temperature of from 275° C. to 375° C. With glass bodies high in silver oxide content, the temperature is generally from about 100° C. to about 200° C., while with glass bodies containing substantial amounts of bismuth oxide, the reduction temperature is usually from about 150° C. to about 250° C.

It appears that the reaction normally begins at the sur-

face of the body exposed to the reducing gas and gradually penetrates into the mass of the material, the penetration depth being dependent, among other factors, on the time and temperature of reduction. The resistance value usually decreases with time since more colloidal metal particles are produced.

The concentration of reducible metal oxides depends upon the resistance value desired for a given shape, the molecular weight of the oxide, etc. Lead oxide, having a high molecular weight and density, may be present in weight concentrations up to about 82%, as for example in a lead silicate flint glass. Bismuth oxide is usually present in concentrations from about 5% to about 55%; antimony oxide is usually present in concentrations from about 5% to about 25%; and silver oxide is usually present in concentrations from 3% to about 20%. When mixtures of these oxides are present, one or more of them may be present in individual concentrations of less than 3%, so long as the total of such oxides is at least 3%.

As indicated above the temperature reduction should be such that the vapor pressure of the reduced metal should be less than 0.0001 mm. This condition obtains when the pressure of the reducing gas is approximately atmospheric. Higher reducing gas pressures may be employed with a corresponding increase in the temperature of reduction.

Innumerable glass compositions are applicable in accordance with the invention. Some of these are listed in the table which follows, along with the resistance value per square under stated conditions of reduction.

| Glass | Composition in percent by weight | Reduction | | Resistance in ohms per square |
|---|---|---|---|---|
| | | Time, hrs. | Temp., ° C. | |
| A | 62% PbO<br>33% SnO<br>5% $Na_2O$ | 3 | 285 | $3\times10^{11}$ |
| B | 52% $SiO_2$<br>18.5% $Na_2O$<br>29.5% $Bi_2O_3$ | 4 | 315 | $6\times10^{8}$ |
| C | 54% $SiO_2$<br>24% PbO<br>23% $Na_2O$<br>29% $Bi_2O_3$ | 10 | 350 | $8.5\times10^{9}$ |
| D | 75% PbO<br>25% $SiO_2$ | 4 | 325 | $1.3\times10^{9}$ |
| E | 68% PbO<br>32% $SiO_2$ | 14 | 310 | $9.8\times10_{9}$ |
| F | 61% PbO<br>37.5% $SiO_2$<br>1.5% $Bi_2O_3$ | 1 | 350 | $8\times10^{12}$ |
| G | 77% $SiO_2$<br>5.5% BaO<br>8.8% $Na_2O$<br>8.7% $Ag_2O$ | 16 | 295 | $6\times10^{11}$ |
| H* | 58% PbO<br>8% $K_2O$<br>34% $SiO_2$ | 8 | 325 | $4\times10^{12}$ |

*Composition H was a vitreous enamel glass applied to a steatite core.

The above examples are intended to illustrate the range of compositions which may be employed in accordance with the various embodiments of the invention. The particular values desired in a finished resistance element can be met by selection of a suitable composition and application of it to the particular structure desired. For example, resistors having a value of $10^{12}$ ohms have been produced by reducing a 3/32" diameter rod of Composition A for 5 hours at 340° C., and cutting the rod into an effective length of 3/4". This element was then heated in a reducing atmosphere until its softening point was reached; at this point, the rod was stretched to a length of 1 inch. Upon cooling, the resistance value was $1.8 \times 10^{12}$ ohms.

As many different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.



What I claim is:

1. An insulated electrical resistance element comprising a sealed tube of glass composed essentially of silica and other metal oxides and containing upon its inner surface from about 3% to about 82% of an oxide selected from the class containing silver oxide, lead oxide, gold oxide, antimony oxide, bismuth oxide and tin oxide, the inner surface of said tube containing colloidal particles of the metals of said oxides, and terminal means for passing an electric current through said metal surface.

2. An insulated electrical resistance element comprising a resistance portion in the form of an elongated self supporting glass member composed essentially of silica and other metal oxides and containing from about 3% to about 82% of an oxide selected from the class containing silver oxide, lead oxide, gold oxide, antimony oxide, bismuth oxide, and tin oxide, only a surface portion of said glass member being chemically reduced to an electrically conductive condition to provide colloidal particles of the metals of said oxides and terminal means for passing an electric current through said metal surface.

3. An insulated electrical resistance element comprising a glass composed essentially of silica and other metal oxides and containing from about 61% to about 75% lead oxide, a surface layer of which contains colloidal particles of lead, and the exposed surface of said surface layer being non-conductive and terminal means for passing an electric current through said reduced layer.

4. A process for producing high resistance value elements which comprises heating in a reducing atmosphere from a temperature of about 75° C. to about 600° C. a solid solution of inorganic metallic oxides containing from about 3% to about 82% of oxides of metals selected from the class consisting of silver oxide, lead oxide, gold oxide, antimony oxide, bismuth oxide and tin oxide, the temperature of reduction being selected so that the vapor pressure of the metals of said oxides does not exceed 0.0001 mm. of mercury, then reoxidizing the exposed surface of said surface layer.

5. An electric circuit component comprising a body of glass having embedded electrically conductive strata generally parallel to each other, at least one of the strata being a chemically reduced glass composed essentially of silica and other metal oxides, and containing from about 3% to about 82% of an oxide selected from the class of silver oxide, lead oxide, gold oxide, antimony oxide, bismuth oxide and tin oxide, said reduced glass being electrically conductive.

6. The invention of claim 5 in which there are two terminal electrode strata and at least one chemically reduced stratum intermediate the terminal electrode strata.


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