

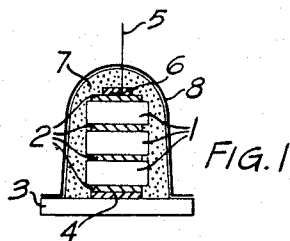
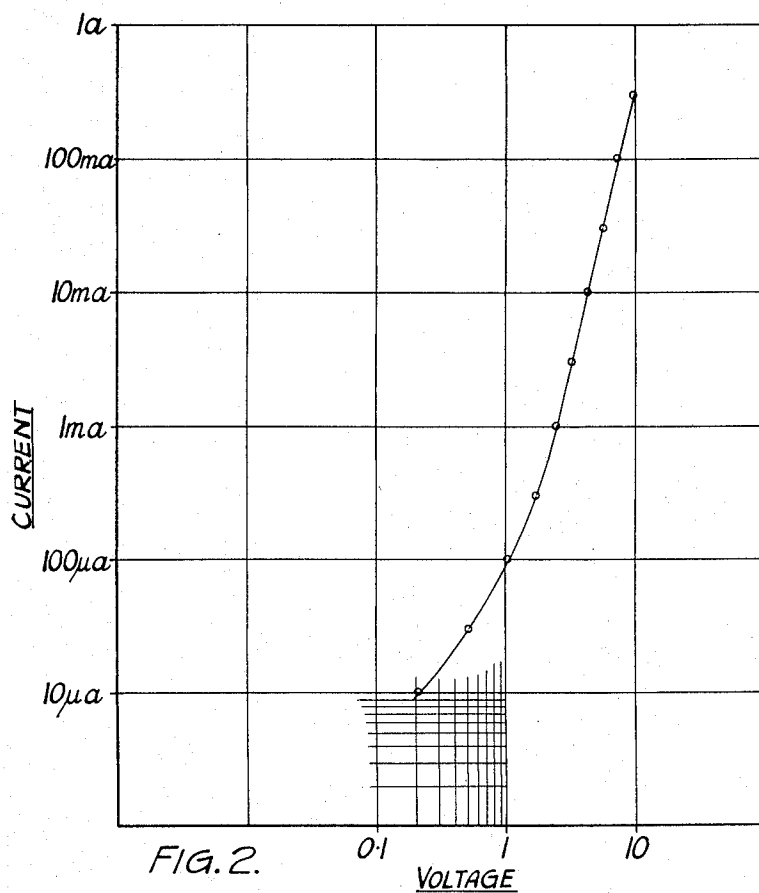
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NON-LINEAR RESISTORS

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2 Sheets-Sheet 1



Inventor:
John Watkins
By Baldwin & Wright
Attorneys

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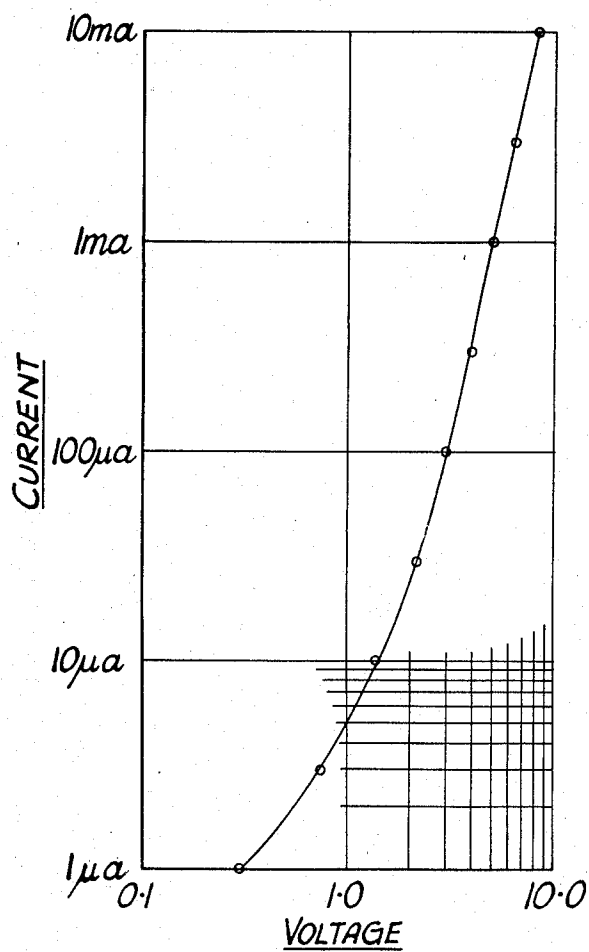
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FIG. 3.



Inventor:
John Watkins
By Baldwin & Wright
attorneys

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NON-LINEAR RESISTORS

John Watkins, Wimbledon, England, assignor to
Morganite Resistors Limited, Durham, England, a
Company of the United Kingdom

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18 Claims. (Cl. 338—115)

This invention relates to low-voltage, non-linear resistors having enhanced performance at audio-frequencies, higher power dissipation and improved electrical stability. Resistors, according to the present invention, are of particular value for use in connection with telephone circuits and may also be used for other applications, such as transistor protection and voltage stabilisation.

According to the present invention a non-linear resistor comprises a fired disc composed of one or more iron oxides with titanium oxide and faced with a fired-on coating of silver, and an electrode attached to or making contact with the silver coating on each face of the disc.

The resistor may include a stack of two or more discs bonded face to face by a suitable conductive bond such as a metallic bond or a graphite based cement, in which case an electrode would be attached to or make contact with each exposed, silver coated end face at the ends of the stack.

Preferably the single or multi-disc assembly is coated with a synthetic resin to increase the mechanical strength thereof, and the thermal emissivity may be increased by applying a black paint to the exterior surface of the resin coating or by incorporating a black pigment in the resin.

One of the electrodes preferably comprises a base plate of, for example, copper adapted to serve as a heat sink. The other electrode may comprise a length of tinned copper wire.

Also according to the invention a method of making a non-linear resistor comprises shaping a powdered composition, containing ferric oxide and titanium oxide, or a material which, on subsequent firing, will deposit titanium oxide, to form a disc, firing said disc in a neutral atmosphere with the result that the ferric oxide is converted to ferrosferric oxide, (Fe_3O_4), coating the faces of the disc with a silver metallising preparation, heating to fire the silver coating and attaching an electrode, if such is provided to the silver coating on each face of the disc. In the case where the resistor comprises two or more discs, electrodes are attached to the exposed, silver coated end faces at the ends of a stack of discs.

With the multi-disc construction of resistor the silver coating applied to the faces of each disc conveniently may serve to bond the discs in face to face relationship, the heating to fire the silver coatings being employed simultaneously to effect said bonding. Alternatively, a multi-disc resistor may be formed by bonding, as a separate operation, a plurality of silver faced discs in face to face relationship with a suitable conducting bonding material, for example, a thermosetting silver paste.

A ferric oxide/titanium oxide mixture suitable for making the discs, may be prepared by careful ball milling, with steel balls, of a mixture of 1 to 10 mol percent titanium oxide and pure ferric oxide ($\alpha\text{-Fe}_2\text{O}_3$), both oxides being of pigment grade. Alternatively, a small amount of a suitable organic titanate, such as butyl titanate, suitably dispersed in an organic vehicle, is mixed with the pure ferric oxide to form slurry which is then dried out at about $1-10^\circ\text{C}$., the butyl titanate decomposing to titanium oxide during the subsequent firing operation. This latter method ensures very complete and uniform dispersion of the titanium oxide in the ferric oxide.

The resulting powder is preferably pre-pressed into

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compacts and these are sintered by firing in air at about 1000°C ., which simultaneously decomposes the butyl titanate, if it is present, to titanium oxide. After sintering, the compacts are crushed to give a powder suitable for repressing. Small discs are then pressed from the powder obtained and fired in a neutral atmosphere such as nitrogen, at about 1300°C ., thereby converting the ferric oxide to ferrosferric oxide. Alternatively and preferably the ferric oxide powder is pressed into blocks, using a little distilled water as binder and these are pre-fired in air at 1000°C . They are then crushed and milled to pass through 100 B.S. sieve. To the resulting powder butyl titanate dispersed in butyl alcohol is added and the slurry is dried out at 160°C ., pressed into small discs and fired at about 1300°C . in a natural atmosphere, which firing decomposes the butyl titanate.

Depending upon the desired characteristics of the resistor, single or multi-disc assemblies are then formed. In the case of a single disc resistor a coating of a suitable high-temperature-setting silver metallising preparation is applied to both faces of the disc which is then fired at a suitable temperature above about 600°C .

In the case of a multi-disc resistor the desired number of such fired silver-coated discs are bonded together in face to face relationship with any suitable conductive bonding means, e.g. a thermosetting silver paste. However, it is preferred to form a multi-disc resistor, simply and conveniently, by applying the high-temperature-setting silver metallising preparation to the faces of a number of discs, stacking said silver faced discs in face to face relationship and heating the stack simultaneously to fire silver coating, and bond the discs together.

After firing of the silver coating electrodes may be connected one to each face of a single-disc resistor or one to each end of a multi-disc resistor, by any suitable conductive bond such as a thermosetting silver paste. The assembly is then preferably coated with a synthetic resin, which may include a black pigment, to increase the mechanical strength thereof and also to protect the resistor from the atmosphere.

As previously mentioned, one of the electrodes, if such are provided, preferably is constituted by a base plate of copper that will serve as a heat sink. Finally, if a black pigment has not been incorporated in the resin, a black paint is applied to the external surface of the resin coating to increase the thermal emissivity of the assembly.

In the drawings—

FIGURE 1 is a diagrammatic, vertical section of a non-linear resistor according to the present invention, and

FIGURE 2 is a graph of the average current/voltage characteristic of resistors made according to Example I, and

FIGURE 3 is a graph of the current/voltage characteristic of a resistor made according to Example II.

Referring to FIGURE 1, three discs 1 composed of a combination of iron oxides and titanium oxide, are bonded in face to face relationship with a high temperature-fired silver metallising preparation 2, and the exposed faces of the two outer discs have a fired coating of said metallising material. An electrode comprising a copper base plate 3, is attached to one end of the assembly of discs by a thermosetting silver paste 4. An electrode comprising a tinned copper wire 5 is attached to the other end of the assembly by a thermo-setting silver paste 6. A coating 7, of a synthetic resin, is applied over the assembly of the bonded discs 1 and a layer 8 of black paint is applied to the exterior surface of said coating 7.

In some constructions of resistors it may not be desired or may be unnecessary to connect electrodes to the end

faces of the resistors and instead, to obtain electrical connection, it is envisaged that spring loaded or biased metal plates or fingers would be arranged to bear against said end faces. In the case where the resistors are coated with resin and black paint, it would, of course, be necessary to keep the end faces or portions thereof free from such coatings.

In the resistors according to the present invention it is believed that the main non-linear action occurs at the inter-faces between the discs and the silver coating and bonding layers. It is believed that thin films or layers of silver titanate are formed at their outer faces during firing of the silver preparation and act as non-linear barriers to give the non-linear characteristics of the resistor at low voltage.

Example I

A slurry was formed by thoroughly mixing 100 gm. of pigment grade ferric oxide ($\alpha\text{Fe}_2\text{O}_3$) with a solution of 7.5 gm. of butyl titanate (35% TiO_2) in 75 ml. of butyl alcohol. The slurry was dried out by heating at 110°C . The resulting powder was then pressed into compacts at a pressure of about 3-5 tons/in.² and they were fired in air at 1000°C . for 1 hour. The compacts were then crushed and passed through a 100 B.S.S. mesh sieve to give a powder.

Discs $\frac{5}{8}$ inch diameter and $\frac{1}{32}$ inch thick were then pressed from the powder and fired in nitrogen (oxygen content less than 10 parts per million) at 1300°C . for 1 hour.

After cooling, three of the discs were bonded together as shown in FIGURE 1, by means of a silver metallizing preparation (Johnson Matthey type Y. 40) and the assembly was fired in air at 720°C . for 1 minute to set the bond.

Electrodes were then fastened to the ends of the assembly. As powers of about 1 watt were expected to be dissipated in a disc during use of the resistor, one electrode was made in the form of a copper base plate, as shown, which also serves as a heat sink. The other electrode was a length of 24 S.W.G. tinned copper wire. Both electrodes were fastened to the assembly by means of a thermosetting silver paste (Johnson Matthey FSP 36) and stoved at 120°C . for 1 hour. A coating of epoxy resin ("Araldite") was then applied and cured at 120°C . for $\frac{1}{2}$ hour. Finally black paint ("Foliac" 384/1) was applied to all surfaces except the bottom face of the plate electrode and the wire electrode.

The current/voltage characteristic of twelve such resistors was measured by recording current against applied voltage and the averaged characteristics is shown in the graph in FIGURE 2 of the accompanying drawing.

Between currents of 1 ma. and 100 ma. the value of n was 3.2 (in the formula $R=KV^{-n}$ where R is the resistance of applied voltage V , K is a numerical constant, and n is the index indicating the degree of non-linearity).

Example II

$\alpha\text{Fe}_2\text{O}_3$ powder was pressed into compacts at a pressure of about 3-5 tons/square inch and prefired in air at 1000°C . for 1 hour. The compacts were crushed and passed through 100 B.S.S. mesh sieve to give a powder. A slurry was then formed by mixing 100 gm. powder with a solution of 7.5 gm. of butyl titanate (35% TiO_2) in 75 ml. of butyl alcohol. The slurry was dried out by heating at 110°C . and the resulting powder was used to form small discs which after a heat treatment of 1 hour at 1300°C . in nitrogen (oxygen content less than 10 p.p. million) had average dimensions of

Diameter	0.51
Thickness	0.083

After cooling, two of the discs were separately coated on both flat sides with a silver metallizing preparation (Johnson Matthey type Y. 40) and the assembly was fired

in air at 720° for 60 minutes to set the bond. After cooling, the discs were bonded together by means of a thermosetting silver paste (Johnson Matthey type FSP49H/FSP49R), and 20 S.W.G. tinned copper wires were joined to the exposed end faces with the same thermosetting silver paste. The paste was cured at 120°C . for 30 minutes. The assembly was then immersed in a mould containing an epoxy resin ("Shell Epikote") to which a small quantity of black pigment (carbon black) had been added and allowed to cure at room temperature for 4 hours.

On extraction from the mould the current/voltage characteristic of the resistor was measured by recording current against voltage and the characteristic is shown in FIGURE 3.

Between currents of 100 μa . and 10 ma. the value of n was 3.3 (in the formula $R=KV^{-n}$ where R is the resistance of applied voltage, K is a numerical constant, and n is the index indicating the degree of non-linearity).

Resistors can be easily made up to meet various requirements by altering either the area of the discs or the number of discs used in the unit.

What is claimed is:

1. A non-linear resistor including a stack of fired discs bonded face to face by a conductive bond, each of said discs being composed of iron oxide with titanium oxide and faced with a fired-on coating of silver and a covering of a synthetic resin around said stack to increase the mechanical strength thereof, said coating having black paint applied to its exterior surface thereby to increase the thermal emissivity.
2. A non-linear resistor including a stack of fired discs bonded face to face by a conductive layer, each of said discs being composed of iron oxide with titanium dioxide and being faced with a fired-on coating of silver, and a coating of a synthetic resin incorporating a black pigment over said stack to increase the mechanical strength thereof.
3. A method of making a non-linear resistor, comprising shaping a powdered composition containing ferric oxide and a material which, on subsequent firing, will deposit titanium oxide, to form a disc, firing said disc in a neutral atmosphere, coating the faces of the disc with a silver metallizing preparation and heating to fire said silver coating.
4. A method according to claim 3 wherein said powdered composition is prepared by mixing pure ferric oxide powder with an organic titanate dispersed in an organic vehicle, to form a slurry and drying out said slurry to provide a powdered composition comprising ferric oxide and an organic titanate.
5. A method according to claim 4 wherein butyl titanate dispersed in butyl alcohol is mixed with said ferric oxide.
6. A method of making a non-linear resistor comprising shaping a powdered composition containing ferric oxide and a material which, on subsequent firing, will deposit titanium oxide, to form several discs, firing said discs in a neutral atmosphere, coating the faces of said discs with a silver metallizing preparation, heating to fire said silver coatings, stacking said discs on each other in face to face relationship and bonding said stacked discs with a conductive bond.
7. A method according to claim 6 including applying an exterior covering of synthetic resin to said stack of discs.
8. A method according to claim 7 including applying a black paint to the external surface of said covering of synthetic resin.
9. A method according to claim 7 wherein said synthetic resin has a quantity of a black pigment incorporated therein.
10. A non-linear resistor having a body comprising a fired disc faced with a fired on coating of silver, said disc being composed of ferrosferric oxide and titanium oxide.
11. A non-linear resistor having a body comprising

a stack of at least two fired discs each faced with a fired on coating of silver, said discs being bonded together by the said silver coatings at the interfaces between the two said discs and each disc being composed of ferrosoferric oxide and titanium oxide.

12. A method of making a non-linear resistor comprising shaping a powdered composition containing ferric oxide and titanium oxide, firing said disc in a neutral atmosphere to convert the said ferric oxide component of the disc to ferrosoferric oxide, coating said disc with a silver metallising preparation and heating to fire the said silver coating.

13. A method according to claim 12 wherein the said powdered composition is prepared by mixing 1 to 10 mol percent titanium oxide and pure ferric oxide, both of said oxides being of pigment grade.

14. A method of making a non-linear resistor comprising shaping a powdered composition containing ferric oxide and a material which on subsequent firing will deposit titanium oxide, to form a disc, firing said disc in a neutral atmosphere to convert the said ferric oxide to ferrosoferric oxide, coating the disc with a silver metallising preparation, and heating to fire the silver coating.

15. A method according to claim 14 wherein the powdered composition comprises pure ferric oxide and butyl titanate.

16. A method according to claim 15 wherein the said powdered composition is prepared by mixing pure ferric oxide powdered with a butyl titanate dispersed in butyl alcohol, to form a slurry and drying out the slurry to provide the said powdered composition comprising ferric oxide and butyl titanate.

17. A method of making a non-linear resistor comprising shaping a powdered composition containing ferric oxide and a material, which, on subsequent firing, will

deposit titanium oxide, to form several discs, coating the faces of said discs with a silver metallising preparation, stacking said discs on each other in face to face relationship, heating said stack simultaneously to fire said silver coating and to bond said discs together, and applying to said stack of discs an exterior covering of a synthetic resin having a quantity of black pigment incorporated therein.

18. A method of making a non-linear resistor comprising shaping a powdered composition containing ferric oxide and a material, which, on subsequent firing, will deposit titanium oxide, to form several discs, coating the faces of said discs with a silver metallising preparation, stacking said discs on each other in face to face relationship, heating said stack simultaneously to fire said silver coating and to bond said discs together, applying to said stack of discs an exterior covering of a synthetic resin, and applying a black paint to the external surface of said covering of synthetic resin.

References Cited in the file of this patent

UNITED STATES PATENTS

905,557	Monasch	Dec. 1, 1908
1,854,926	Broske	Apr. 19, 1932
1,883,840	Wiegand	Oct. 18, 1932
1,927,894	Krause	Sept. 26, 1933
2,289,211	Ridgway	July 7, 1942
2,590,894	Sanborn	Apr. 1, 1952
2,798,010	Bender	July 2, 1957
2,843,914	Koury	July 22, 1958
2,933,710	Novak et al.	Apr. 19, 1960
2,934,736	Davis	Apr. 26, 1960
2,940,941	Dalton	June 14, 1960
3,023,390	Moratis et al.	Feb. 27, 1962