

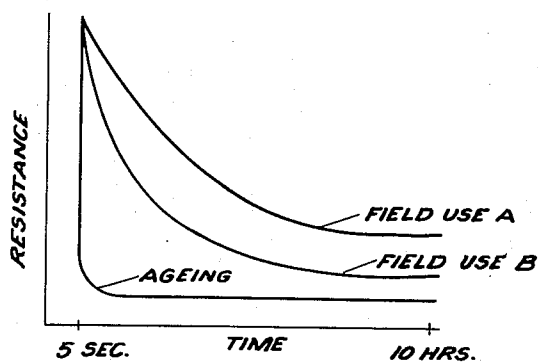
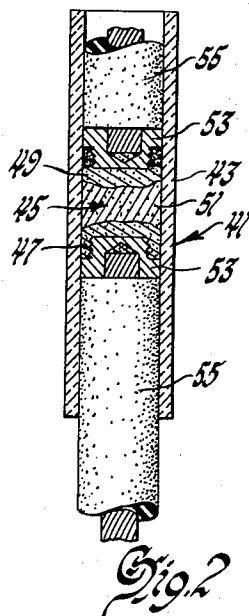
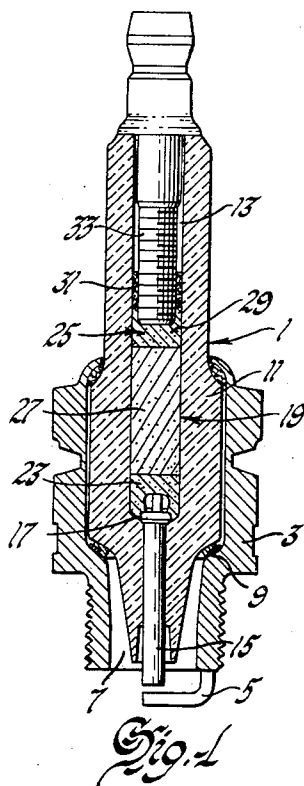
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RESISTOR AND SPARK PLUG EMBODYING SAME

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RESISTOR AND SPARK PLUG EMBODYING SAME

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This invention relates to resistors and particularly to glass phase semi-conductor resistor elements suitable for use in wiring harness and spark plugs of the automotive and aviation type. Resistors are commonly used in such manner to suppress the high frequency oscillations present with spark discharge with ignition system, which oscillations result in rapid erosion of plug electrodes and interference with electronic equipment.

Our invention is an improvement over the monolithic resistor plug described and claimed in the McDougal, Schwartzwalder and Rulka Patent #2,459,282, granted January 18, 1949. This patent discloses a resistance element comprising a heterogeneous mixture of conductor material i. e. carbon either alone or in combination with various conducting metals, metal oxides and metal carbides, with glass. In this composition, the conducting material exists as a continuous phase and the resistance thereof is dependent solely on the amount of conductor material present, the glass serving only to suspend the conductor material in a rigid structure.

Experience with the above type of resistor element has revealed a number of difficulties tending to seriously limit its application. Such resistor elements are limited to use at temperatures below about 500° F. It has been found that the carbon conductor therein oxidizes at a very low temperature, about 500° F., and is subject to very rapid destruction at higher temperatures. Thus, if any arcing or flashover should occur either internally or over the surface of the resistor, or if the operating temperature should rise above about 500° F. due to momentary overload or ambient temperature conditions, the carbon is burned out very quickly and creates a very high resistance with resultant failure of the system.

Since present day engine operating conditions are increasingly severe this carbon type resistor plug is limited to use in special application. Likewise, since arcing and internal flashover is most likely to occur at and between the resistor contact surfaces, these resistors are by the very nature of the manufacturing methods used in their production highly susceptible to failure. Normal manufacturing variables, as are encountered in any well controlled high volume production line, result in variations of temperature and pressure as well as faults in the insulator centerbore which in turn produce resistor elements highly susceptible to arcing and flashover.

A further problem associated with such resistor elements is the lack of stability of the electrical characteristics, i. e., the voltage coefficient and temperature coefficient of resistivity.

It is therefore an object of our invention to provide a resistor element having stable electrical characteristics. It is another object of our invention to provide a resistor element capable of withstanding high operating temperatures. It is another object of our invention to provide a spark plug having stable electrical characteristics and capable of withstanding high operating temperatures.

To attain these objects we provide a resistor comprising a semi-conductor material in admixture with glass with

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or without the addition of small amounts of reducer material, the mixture being hot pressed to form a non-porous resistor element having a gas tight sealing bond with the containing ceramic insulator.

Further objects and advantages of the present invention will be apparent from the following description, reference being had to the accompanying drawing, wherein a preferred embodiment of our invention is clearly shown.

In the drawing:

Figure 1 is a vertical cross-sectional view of an automotive type spark plug embodying our invention.

Figure 2 is a section through a resistor suitable for use in an aviation type ignition harness.

Figure 3 is a graph of resistance against time illustrating the aging of the resistor of our invention as embodied in automotive and aviation type plugs.

Having reference to Figure 1 there is shown an automotive type spark plug comprising a shell 3 provided with screw threads at its lower end for having threaded connection with the engine, a ground electrode 5 being secured to its lower edge. The shell 3 is provided with a stepped centerbore 7 forming an internal ledge 9 therein. Positioned on the ledge 9 is an insulator 11 formed preferably of sintered aluminum oxides, other type materials being possible, the insulator being secured in gas tight relationship with the shell 3.

The insulator 11 is provided with a stepped centerbore 13 adapted to receive and position a center electrode 15 on the ledge 17 formed therein. The electrode 15 may be formed of any suitable material capable of withstanding high temperatures and possessing good heat conductivity. Positioned in the centerbore and overlying the electrode 15 is the resistor section 19. The section 19 has good electrical contact with the electrode 15 and is in gas tight sealed relationship within the insulator 11. The resistor section 19 comprises a lower conducting seal 23, an upper conducting seal 25 and an intermediate portion 27 constituting the resistance element of our invention. The conducting seals may be made of any suitable material capable of being bonded to the insulator and to the resistance element and possessing good electrical conductivity. We prefer to use a mixture of glass and conducting material as described and claimed in Schwartzwalder and Kirk Patent 2,106,578, granted January 25, 1938, and Schwartzwalder and Rulka Patent 2,248,415, granted July 8, 1941.

The lower seal 23 is subjected to greater heating during operation of the plug than is the upper seal 31 and is preferably made from a mixture of boro-silicate glass and powdered copper, the plasticity thereof being such as to preclude its running down over the lower surfaces of the center electrode 15 during the hot pressing operation. The upper seal 25 is formed of a lower portion 29 and an upper portion 31, the lower portion 29 being relatively stiff on hot pressing in order to serve as a plunger for evenly compressing the intermediate portion 27. Both sections 29 and 31 are likewise formed of a mixture comprising powdered copper in glass.

In an effort to find a resistor material having the least possible variation in resistance over the temperature and voltage range encountered in normal operation as well as one capable of withstanding temperatures as high as 1000° F., we have discovered a series of semi-conductor compositions which are basically titanates and stannio-titanates which have been modified to obtain semi-conductor materials having stable and reproducible electrical characteristics, i. e., resistance, low thermal coefficient of resistivity and low voltage coefficient of resistivity.

We have found that the presence of Ta⁺⁵ reduces the resistivity of the titanate and stannio-titanate material to a marked extent. Ta⁺⁵ has about the same ionic radius as Ti⁺⁴ but has a higher ionic charge and is visualized as

going into the titanium crystal structure and forming "holes." It has been found that as little as 2% of Ta_2O_5 lowers the resistivity considerably and the addition of said compound in the amount of 10% reduces the resistance to $\frac{1}{10}$ of that without the addition. Such addition was found to have no effect on the voltage coefficient of resistivity of the composition.

It was also found that V_2O_5 acts in a manner similar to Ta_2O_5 though to a lesser degree. For this reason we prefer to use Ta_2O_5 .

We have also found that the presence of molybdenum or tungsten oxides, alone or in combination, in the titanate or stannio-titanate compositions greatly reduced the voltage coefficient of resistivity. We prefer to use the molybdenum oxide inasmuch as its effect on the voltage coefficient is greater than that of the tungsten oxide.

In order to obtain the characteristics desired, it is necessary to thermally react the semi-conductor constituents. However, it has been found that the reacted composition was not as stable as required for some applications. Stability has been attained by the introduction of certain ceramic materials into the mixture prior to calcination. Such materials as tabular corundum, magnesia, mullite, zircon, chrome oxide, etc., have been found to be suitable. We prefer to use tabular corundum, a high temperature calcined alumina, on the basis of results obtained from test.

The range of compositions yielding the best results are as follows:

Material:	Limits, parts
TiO_2 -----	15-60
SnO_2 -----	0-50
Ta_2O_5 -----	Up to 15
MoO_3 -----	0-10
Al_2O_3 -----	20-40

The preferred composition varies with the particular application in mind. As an example, where the semi-conductor material is to be utilized in a resistor the composition may be

	Parts
TiO_2 -----	60
SnO_2 -----	20
Ta_2O_5 -----	10
MoO_3 -----	4
Al_2O_3 -----	40

The semi-conductor material may be prepared by thoroughly mixing the materials and granulating the mix to pass a 325 mesh (43 micron) screen followed by sintering at a temperature of about 1400° C. in an atmosphere that may be slightly oxidizing. The material thus prepared is then mixed with glass to form a semi-conductor composition which is suitable for application as the resistance element in a monolithic type spark plug or a resistor as hereinafter described. The resistor element so formed is both stable electrically and possesses a dense, substantially non-porous physical structure ideally suited for the applications specifically disclosed.

In accordance with our invention, the use of a barium-borate glass in admixture with our semi-conductor material yields a structure which has a very low range of electrical resistance whereas the use of an alkali-boro-silicate glass yields a structure which has a very high range of resistance. However, a magnesium-borate glass, in contrast to the barium-borate, gives a high range of electrical resistance. Likewise, a boro-aluminum-silicate glass has a very high range of resistance. Thus, it can be seen that the coarse resistance range can be varied widely by a change in composition of the glass phase. Likewise, as pointed out hereinbefore, coarse control of the resistance of the composition is obtained by varying the amount of Ta_2O_5 in our semi-conductor material.

The fine control of the resistance of our final composition is obtained by the addition of reducing agents, the resistance being lowered as the amount of reducer is in-

creased. We have found that the addition in very small quantity of such reducing agents as powdered aluminum and carbon, the latter having a particle size of about 0.3 micron and being available commercially as Thermax, enables almost precision-like control of the resistance of the final product. The amount of reducer added should be so small as to exist in the product as a discontinuous phase and function not as a conductor material but solely as a reducing agent. Though the exact nature of the chemical and physico-chemical interaction of the materials in the composition is not known, it is theorized that the glass phase acts to form a multitude of reaction bombs, each containing reducer and semi-conductor material which reacts in the course of hot pressing to form a glass-like semi-conducting structure. The reaction in the glass-phase apparently also results in the materials being integrated therewith.

We have found that the amount of the particular glass used, as distinguished from the amount of reducer used, has no appreciable effect on the resistance of the composition within the limits of about 25 to 40 parts by weight of the composition. Likewise, though the composition of the glass phase does not effect the temperature coefficient of resistivity or voltage coefficient of resistivity of the semi-conductor composition, it is undesirable to mix two or more types of glass since we have found that such mixing tends to reduce the stability of the temperature and voltage coefficients otherwise obtained.

The fluidity of the final composition, as exhibited during the hot pressing operation, is controlled by the presence of a filler or diluent material which does not react chemically with the other constituents of the composition. We have been able to obtain very satisfactory results with a -48 to +100 mesh mullite though other materials such as borolon, zircon, chromium oxide and aluminum oxide, etc. may be used. The filler or diluent material may be added to the semi-conductor composition or may be only that amount present in the semi-conductor (stannio-titanate) material. It has been noted that the filler also increases the temperature resistance of the formed element after hot pressing, the composition becoming more refractory and less fluid than on the first heating.

Since the glass phase semi-conductor composition is best handled in a granulated form, a binder such as bentonite, a very plastic aluminum silicate, is added to bond the particles together during processing.

The range of composition may vary widely depending on the electrical, thermal and voltage characteristics desired. We have found the following range to be suitable for most purposes:

	Parts
Glass -----	25-40
Semi-conductor material -----	25-75
Filler -----	0-40
Reducing agent -----	0-6

The preferred composition varies with the particular application in mind and the following are examples of compositions preferred for use in resistors:

Resistance (approximate)----- ohms--	1,000	10,000
Glass (Barium-borate type)----- parts--	25	-----
Glass (Magnesium-borate type)----- do--	-----	25
Semi-conductor material ----- do--	45	50
Filler ----- do--	30	25
Aluminum ----- do--	0.8	1
Carbon (Thermax) ----- do--	0.8	1
Bentonite ----- do--	3	3

The semi-conductor composition of our invention may be prepared in granular form by first dry mixing the materials and then adding water to make a plastic mass. The plastic mass is then forced through a 20 mesh screen and the resulting granules dried. The dried material is then regranulated through a 28 mesh screen and the

material retained between 28 and 100 mesh is used. This sizing has been found to produce granules which are most suitable for uniform volumetric feed. Alternatively, the materials may be dry mixed and formed into a free-flowing slip by addition of water. The slip is then passed into a spray-drying tower where the desired agglomerates are formed.

In assembling the plug 1, the center electrode 15 is positioned within the centerbore 13 of the insulator 11 and a measured amount of copper-glass seal is fed into the bore and rammed in place. Any loose powder is blown out of the insulator to prevent contamination of the intermediate resistor portion 27. The desired amount of powdered resistance material is then placed in the bore and rammed, followed by a measured amount of powdered copper-glass seal material 29 which is likewise rammed to form the lower portion 29 of the upper conducting seal 25. A small quantity of copper-glass material is then loaded into the insulator followed by ramming to form the upper portion 31 of conducting seal 25. A terminal screw 33 is then positioned within the bore and the whole assembly is heated to a temperature of from 1550° F. to 1850° F., depending on the type of glass used. When the glass is sufficiently softened, pressure is applied to the terminal screw 33 to force it down into the bore, thereby compressing the softened materials and causing the upper seal portion 31 of upper seal 25 to surround and grip the lower end of the screw. In this manner, a continuous electrical path is formed through the plug from the terminal screw 33 to the center electrode 15, the portions intermediate the top of the electrode and the bottom of the screw being sealed in gas tight relationship with the wall of the insulator and the metal parts. The thus formed insulator assembly is then assembled in shell 3 to form plug 1.

In Figure 2 there is shown a resistor 41 embodying the resistor element of our invention. The resistor 41 consists of an insulator sleeve 43 of either sintered alumina or porcelain, as in the case of insulator 11, having a resistor section 45 comprising a lower conductive seal 47, an intermediate resistor portion 51 and an upper conducting seal 49, likewise as shown and described with reference to Figure 1. Secured within the ends of the glass seals 47 and 49 are a pair of metal terminals 53, each of which is connected to an ignition cable 55 in the ignition harness or other electrical circuit. The cables 55 are secured within the terminals 53 in any suitable manner well known in the art. The glass seals 47 and 49 form a good electrical bond with the terminal 53 in a manner similar to that shown and described with reference to Figure 1.

The method of manufacture of this resistor 41 is substantially the same as that described above for plug 1. One of the terminals 53 is inserted in the sleeve 43, the glass seal material is inserted, followed by the powdered resistance material and the second seal material. The other terminal 53 is then inserted and the assembly is heated to soften the glass, pressure being then applied to the terminals to cause them to seat in the glass as shown and to compress the conducting seals and the resistance portion 47, 51 and 49, respectively. Suitable stops are provided in the hot pressing operation to center the resistor section 45 within the sleeve 43.

We have found that it was desirable to subject the resistor elements of our invention to an electrical aging process prior to actual field use in order to completely stabilize the resistance. The aging process we have reference to comprises subjecting the resistor element to electrical treatment wherein the peak power dissipated in the element is higher than that encountered in field use. Thus we preclude a gradual and prolonged decrease in resistance. The aging treatment reduces the resistance to a value that will remain substantially constant over long periods of use in the field.

It has been found that the decrease in resistance is a function of the peak power dissipated in the resistor element and that the resistance tends to stabilize at a value characteristic of the peak power of the operating circuit. Thus, in an engine circuit giving 0.01 joule per spark, the resistor will stabilize at a higher value than it would at 10 joules per spark and would not, even on continued operation, drop to the latter value.

Having reference to Figure 3, there is shown in the upper and lower curves the behavior of an automotive spark plug such as shown in Figure 1 when used in the field without the benefit of aging treatment in the manufacturing process and when subjected to aging prior to field use. These curves are respectively designated on the graph as Field Use A and Aging. As is clearly shown, the plug on being subjected to aging treatment drops off very sharply in resistance and stabilizes at a value characteristic of the peak power used. The plug subjected to aging in field use merely decreases in resistance gradually and over a long period of time, finally producing a plug having a resistance value higher than that resulting from the aging treatment since the peak power used in aging is higher than that normally encountered in the field. It should be noted, that even after a stabilized value in field use aging has been obtained, such value is subject to change upon momentary overloading of the circuit which subjects the plug to a new peak power value. The disadvantages of a plug having to age during its early stages of field operation are thus readily apparent. The intermediate curve, designated as Field Use B, represents the aging characteristics of a plug used in an internal combustion aviation engine. The characteristics are generally the same as those discussed above with reference to the Field Use A curve. As is clearly shown, however, the stabilized resistance value for the B curve is less than that for the A curve since the aviation engine normally operates at a higher peak power value than does the automotive engine.

It is thus clear, from the above description, that we have provided resistors and plugs having stabilized electrical characteristics and capable of use at high operating temperatures. It should be understood that though the original semi-conductor material, the stannio-titanate calcine, has certain inherent electrical properties, these have been modified by the physical, thermal and electrical treatments to which it was subjected. Specifically, the grinding of the calcine, the admixture thereof with glass together with, if desired, reducing materials and finally reacting the materials under heat and pressure all combine to fundamentally alter the electrical characteristics of the original materials.

While we have disclosed our invention with reference to certain preferred embodiments thereof, it is to be understood that modification may be made within the limits of our disclosure and as defined by the scope of the attached claims which follow.

What is claimed is:

1. A resistor comprising the combination of an insulator sleeve, a metal conducting member positioned in said sleeve, a glass conducting seal overlying said member and having a gas-tight bond with said sleeve, a semi-conductor overlying said seal and being bonded thereto and to said sleeve, a second glass conducting seal overlying said semi-conductor and being bonded thereto and to said sleeve, and a second metal conducting member in said sleeve having good electrical connection with said second seal, said semi-conductor being formed of a composition comprising 25 to 40 parts glass, 25 to 75 parts semi-conductor material, 0 to 40 parts filler and 0 to 6 parts reducing agent, said resistor having substantially stabilized resistance.

2. A resistor in accordance with claim 1, wherein said semi-conductor consists essentially of about 25 parts barium borate glass, about 45 parts semi-conductor mate-

rial, about 30 parts filler, about 0.8 part aluminum and about 3 parts bentonite.

3. A resistor in accordance with claim 1, said semi-conductor consisting of about 25 parts magnesium borate glass, about 50 parts semi-conductor material, about 25 parts filler, about one part aluminum and about 3 parts bentonite.

4. A resistor in accordance with claim 1, said semi-conductor comprising 25 parts barium-borate glass, 45 parts semi-conductor material, 30 parts filler, 0.8 part aluminum, 0.8 part carbon and 3 parts bentonite.

5. A resistor in accordance with claim 1, said semi-conductor comprising 25 parts magnesium-borate glass, 50 parts semi-conductor material, 25 parts filler, 1 part aluminum, 1 part carbon and 3 parts bentonite.

6. A device of the type described comprising the combination of a tubular insulator, a metal conducting member positioned in said insulator, a semi-conductor overlying said member in good electrical connection therewith and being bonded to said insulator, and a second metal conducting member in said insulator having good electrical connection with said semi-conductor, said semi-conductor being formed of a composition comprising 25 to 40 parts glass, 25 to 75 parts semi-conductor material, 0 to 40 parts filler and 0 to 6 parts reducing agent.

7. A device of the type described comprising the combination of a tubular insulator, a metal conducting member positioned in said insulator, a glass conducting seal overlying said member and having a gas-tight bond with said insulator, a semi-conductor overlying said seal and being bonded thereto and to said insulator, a second glass conducting seal overlying said semi-conductor and being bonded thereto and to said insulator, and a second metal conducting member in said insulator having good electrical connection with said second seal, said semi-conductor being formed of a composition comprising 25 to 40 parts glass, 25 to 75 parts semi-conductor material, 0 to 40 parts filler and 0 to 6 parts reducing agent, said semi-conductor material comprising 15 to 60 parts titanium oxide, 0 to 50 parts tin oxide, up to 15 parts of a metal oxide selected from the group consisting of tantalum oxide and vanadium oxide, 0 to 10 parts of at least one metal oxide selected from the group consisting of molybdenum oxide and tungsten oxide, and 0 to 40 parts of a material selected from the group consisting of tabular corundum, magnesia, mullite, zircon and chrome oxide, said semi-conductor having substantially stabilized resistance.

8. A device of the type described herein comprising the combination of a spark plug insulator having a center-bore formed therein, a center electrode member positioned in said insulator, a glass conducting seal overlying said member and having a gas-tight bond with said insulator, a semi-conductor overlying said seal and being bonded thereto and to said insulator, a second conducting seal overlying said semi-conductor and being bonded thereto and to said insulator, and a terminal screw in said insulator having good electrical connection with said second seal, said semi-conductor being formed of a composition comprising 25 to 40 parts glass, 25 to 75 parts semi-conductor material, 0 to 40 parts filler and 0 to 6 parts reducing agent, said semi-conductor having substantially stabilized resistance.

9. A device in accordance with claim 8 wherein the resistor is formed of a composition consisting of about 25 parts barium borate glass, about 45 parts semi-conductor material, about 30 parts filler, about 0.8 part aluminum and about 3 parts bentonite.

10. A device in accordance with claim 8 wherein the resistor is formed of a composition consisting of about 25 parts of magnesium borate glass, about 50 parts semi-conductor material, about 25 parts filler, about one part aluminum and about 3 parts bentonite.

11. A device in accordance with claim 8 wherein the resistor consists of a composition comprising 25 parts of barium-borate glass, 45 parts semi-conductor material, 30 parts filler, 0.8 part aluminum, 0.8 part carbon and 3 parts bentonite.

12. A device in accordance with claim 8 wherein the resistor consists of a composition comprising 25 parts of magnesium-borate glass, 50 parts semi-conductor material, 25 parts filler, 1 part aluminum, 1 part carbon and 3 parts bentonite.

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