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RESISTOR COMPOSITION

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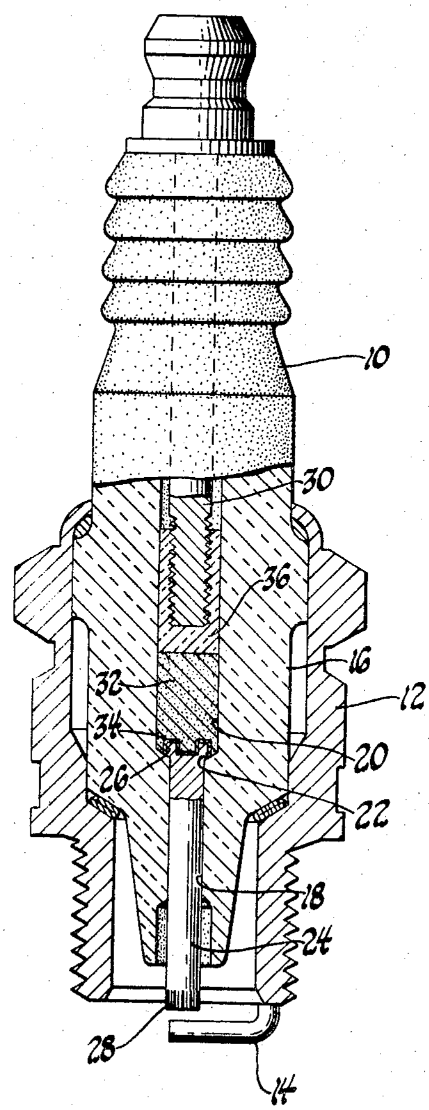

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RESISTOR COMPOSITION

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ABSTRACT OF THE DISCLOSURE

An improved resistor composition for use in resistor spark plugs and other electrical devices is disclosed. The resistor composition contains a metal powder taken from the group consisting of zinc, antimony and tellurium in addition to the conventional resistor composition ingredients. The metal, for example, zinc, causes the resistor mass to bond tightly to the center electrode head in the spark plug insulator centerbore.

This invention relates to resistors, and more particularly to glass phase semiconductor resistor compositions suitable for use in resistors and resistor spark plugs of the automotive aviation type.

Resistors are commonly used to suppress the high frequency oscillations present with spark discharge in an ignition system, the oscillations resulting in rapid erosion of the spark plug electrodes and in interference with electronic equipment. Resistor spark plugs are effective in reducing automobile radio frequency interference and are particularly useful for FM broadcast and shortwave broadcast automobile receivers.

There are two basic types of resistor compositions. One type of monolithic resistor spark plug described in the McDougal et al. Pat. No. 2,459,282 granted Jan. 18, 1949, comprises a heterogeneous mixture of conductor material, that is, carbon either alone or in combination with various conducting metals, metal oxides and metal carbides with glass. In this type of resistor the conducting material, such as carbon, exists as a continuous phase and the resistance of the resistor is dependent solely upon the amount of conductor material that is present. The glass serves only to suspend the conductor material in a rigid structure. An example of this type resistor composition consists essentially of 64 weight percent borosilicate glass, 9 weight percent magnesium borate glass, 11 weight percent fluorspar, 15% beryl and 1% thermax carbon.

The second basic type of monolithic resistor spark plug is described in the patent to Counts et al., No. 2,864,884 granted Dec. 16, 1958, and No. 3,235,655 granted Feb. 15, 1966. This type of resistor consists of a semiconductor material with glass and a small amount of reducing agent such as powdered aluminum or carbon. In this type of resistor, the semiconductor material exists as a continuous phase and the resistance of the resistor is dependent mainly upon the resistance characteristics of the semiconductor material that is present. In this type of resistor, the amount of reducing agent, that is carbon or powdered aluminum and the like, are added to obtain precision-like control of the resistance of the final product, but the amount of reducing agent added should be small so that it is present in the product in a discontinuous phase and, as a result, does not function as a conductor material but solely as a reducing agent. An example of this type of resistor composition consists essentially of 25 parts barium borate glass, 30 parts filler (mullite), 0.8 part aluminum, 0.8 part thermax carbon black, 3 parts bentonite and 45 parts of a semiconductor composition containing 60 parts TiO_2, 20 parts SnO_2, 10 parts Ta_2O_5, 4 parts MoO_3 and 40 parts Al_2O_3.

These two basic types of spark plug resistors described

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above have been improved by the addition of a water soluble, charable carbon containing material so that they are substantially resistant to change when subjected to electrical aging or field use. This is described fully in the copending patent application Ser. No. 670,178, assigned to the assignee of the present patent application.

All of the resistor compositions referred to above are positioned in the spark plug centerbore of a resistor spark plug between two electrical conductive glass seals. One conductive glass seal bonds tightly to the center electrode head and the other conductive glass seal bonds tightly to the lower end of the terminal screw. It is necessary to use the conductive glass seals on either side of the resistor seal because the resistor seals of the type described above do not bond tightly to and maintain good contact with the center electrode head and/or the terminal wire. Resistor spark plugs employing a resistor seal position between the two electrical conductive glass seals are typically referred to as three-load resistor plugs.

It is the primary object of this invention to provide an improved resistor composition. It is another object of this invention to provide a resistor composition which will bond tightly to the center electrode head and maintain good contact therewith to provide a stable spark plug resistance over a long period of time. It is another object of this invention to provide a two load resistor spark plug.

These and other objects are accomplished by a resistor composition containing a metal taken from the group consisting of zinc, antimony and tellurium in addition to the conventional resistor composition ingredients. The resistor composition in accordance with this invention consists essentially of 20 to 75 weight percent glass, 15 to 80 weight percent inert filler, 0 to 60 weight percent semiconductor, 0 to 3.0 weight percent inorganic binder, 0.1 to 4.0 weight percent carbon black, 0.1 to 4.0 water soluble, charable carbon containing material and either 2 to 15 weight percent of a metal taken from the group consisting of zinc and antimony or 0.5 to 5.0 weight percent tellurium. When a spark plug having a resistor composition of this type positioned above and around the nickel center electrode head is heated and pressed with a terminal screw, as is the practice in the art, the resulting fused mass forms a resistor seal which bonds tightly to the center electrode head and which has a stabilized resistance for an extended period of time. The metal taken from the group cosisting of zinc, antimony and tellurium alloys with the nickel center electrode head to form a metal-nickel alloy coating thereon which enable the resistor composition to bond tightly to the center electrode head thereby eliminating the need for the lower conductive glass seal normally found in the prior art three-load resistor spark plugs.

Other objects and advantages of this invention will be apparent from the following detailed description, reference being made to the accompanying drawing wherein a preferred embodiment of this invention is shown.

Referring now to the drawings, the spark plug **10** comprises a conventional outer metal shell **12** having a ground electrode **14** welded to the lower end thereof. Positioned within the metal shell **12** and secured in the conventional manner is the insulator **16**. The ceramic insulator **16** should preferably be of a high aluminum base material containing upwards of 85% aluminum oxide such, for example, as covered by U.S. Pat. No. 2,760,875, issued to Karl Schwartzwalder and Helen Blair Barlett. The insulator **16** is formed with a centerbore having a lower portion **18** of relatively small diameter and an upper portion **20** of larger diameter which are connected by the insulator centerbore ledge **22**. Positioned in the lower portion **18** of the insulator centerbore is the conventional nickel center electrode **24**. The center electrode **24** is preferably nickel although other metals which can be coated with zinc, antimony or tellurium may be used. The center electrode **24** has an enlarged head **26** at the upper end thereof which rests on the inner insulator centerbore ledge **22** and a serrated lower end **28** thereof projecting beyond the lower tip of the insulator **16**. Positioned in the upper portion **20** of the insulator centerbore is a terminal screw **30**. The monolithic resistor element or seal **32** of this invention which will be hereinafter fully described is positioned in the insulator centerbore **20** and is bonded to the center electrode head **26** and to the inner walls of the ceramic insulator. The center electrode **26** has a metal coating **34** thereon which will be hereinafter also fully described. Positioned on top of the resistor seal **32** in the insulator centerbore **20** is a conductive metal-glass seal **36**. The conductive metal-glass seal **36** is bonded to the terminal screw **30** and the inner walls of the ceramic insulator.

The conducting metal-glass seal **36** 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 materials as described and claimed in the Schwartzwalder et al. Pats. No. 2,106,578 granted Jan. 15, 1938 and No. 2,248,415 granted July 8, 1941, in the Blum et al. Pat No. 3,349,275 granted Oct. 24, 1967 and in the copending patent application Ser. No. 563,775 assigned to the assignees of this invention. An example of a conducting metal-glass seal is a composition containing 50 parts copper powder, 14 parts zinc powder, 1 part of an organic binder such as hydrogenated cottonseed oil and 35 parts of a borosilicate glass containing 65 weight percent SiO_2, 23 weight percent B_2O_3, 5 weight percent Al_2O_3, and 7 weight percent Na_2O. The conductive glass seal **36** together with the resistor seal **32** provides an electrical conductive path from the terminal screw **30** to the center electrode **24**.

In accordance with the present invention, the spark plug resistor seal **32** is a dense, fused mass containing glass, insert filler material, carbon, inorganic binder, a water soluble charable carbonaceous material and a metal taken from the group consisting of zinc, antimony and tellurium. The composition of the resistor seal **32** of our invention may be formed of the following constitutents in the percent by weight noted.

	Wt. percent
Glass	20 to 75
Inert filler—kyanite, borolon, zirconia, mullite, chromium oxide, and the like	15 to 80
Semiconductor material	0 to 60
Carbon black	0.1 to 4.0
Inorganic binder—Bentonite (clay)	0 to 3
Water soluble charable carbon containing material-dextrin, sucrose, methyl cellulose, corn flour, polyvinyl alcohol, glycerin	0.1 to 4.0
Zinc, antimony (tellurium)	2 to 15 (0.5 to 5.0)

The glass used in the spark plug resistor seal **34** may be any conventional glass commonly used in spark plug seals. Barium borate glasses are preferred although this invention is not limited thereto. An example of a suitable barium borate glass is a composition containing 75 weight percent B_2O_3 and 25% BaO. Another barium borate glass is a composition containing 60 weight percent B_2O_3, 32 weight percent BaO, 6 weight percent Na_2O and 2 weight percent CaO. Another example is a composition containing 60 weight percent B_2O_3, 38 weight percent BaO and 2 weight percent Na_2O. It has been found that the amount of the particulate glass used has no appreciable effect on the resistance of the composition within the limits of 20 to 75 weight percent.

The fluidity of the final resistor composition, as exhibited during the hot pressing operation, is controlled by the presence of a filler which does not react chemically with the other constituents of the resistor composition. These fillers may be selected from the broad group of filler materials commonly used in resistor glass seals. Examples of suitable fillers are kyanite, alumina, zirconia, mullite, borolon and the like. A preferred filler is a mixture of 25 parts by weight kyanite and 35 parts by weight zirconia. The concentration of the filler is from about 25 to 80 weight percent.

Since the resistor 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. Inorganic binders such as bentonite, as well as other clays, may be used. Organic binders are not recommended for the practice of this invention since it is well known in the art that this type of material causes the resistance of the resistor to be unstable. The concentration of the binder is from 0.0 to 3.0 weight percent.

The concentration of the carbon black in the resistor composition is from about 0.1 to 4.0 weight percent. The carbon black may function as the sole conductor material for resistors of the type described in the McDougal et al. Pat. No. 2,459,282 previously referred to, or solely as a reducing agent as in the resistors of the type described in the Counts et al. Pat. No. 2,864,884.

A water soluble, charable carbonaceous material such as dextrin, sucrose, methocel, corn flour, polyvinyl alcohol and glycerine is incorporated into the resistor mass in a concentration so that this material combines with the carbon black and/or semiconductor material to provide a resistor mass which is resistant to electrical aging. The use of water soluble, charable carbonaceous material in resistors is described in the copending patent application SN 670,178 assigned to the assignees of the present invention and is incorporated herewith by reference. The concentration of the water soluble, charable carbonaceous material in the resistor composition is from about 0.1 to 4.0 weight percent.

It has been found that a metal powder taken from the group consisting of zinc, antimony and tellurium in a resistor composition enables the resistor mass to bond tightly to the nickel center electrode head. These metals, zinc, antimony and tellurium, have relatively low melting points which are 788° F., 1258° F. and 846° F., respectively. The melting points of these materials are lower than the temperature encountered during the assembly of the spark plug, thereby indicating that these metals are most likely in a liquid state during the pressing of the terminal screw step in the assembly of the resistor plug. It is believed, although this invention is not limited to this theory, that the metal powder melts and while it is in a liquid state, it either forms a metal coating for example, zinc, or a metal alloy coating, for example, zinc-nickel on the center electrode head. A substantial portion, for example 70 to 80 percent, of the metal in the resistor composition migrates to the two ends of the composition, thereby making a portion of the metal readily available for coating the center electrode head. This coating lessens oxidation of the center electrode and is wetted by the fluid glass seal more effectively during the pressing operation. As a result, a weak-to-strong bond between the resistor glass seal phase and the center electrode is formed. Resistor compositions which are substantially identical except that they do not contain the metal powders referred to above do not adhere to the center electrode whereas when one of these metal powders is present, the resistor composition does adhere to the electrode. One advantage of such a system is that one of the conductive glass seals can be eliminated thereby reducing the manufacturing costs. The particle size of the metal powder is not critical in the practice of this invention as long as a uniform resistor compositon can be made. The concentration of the zinc or the antimony is 2 to 15 weight percent with the preferred concentration being about 3 to 7 weight percent. The concentration of the tellurium is 0.5 to 10.0 weight percent with the preferred concentration being 4 to 5 weight percent.

The resistor compositions of this 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 procedure has been found to produce granules which are most suitable for uniform volumetric feed in the mass production of resistor spark plugs. Alternatively, the materials may be dry mixed and formed into a free-flowing slip by the addition of water. The slip is then passed into a spray drying tower where the desired agglomerates are formed.

In assembling the spark plug **10**, the center electrode **24** is positioned within the centerbore **18** of the insulator **16**. The desired amount of the granulated resistor composition **32** is then placed in the centerbore on top of the center electrode head **26** and rammed, followed by a measured amount of the powdered copper-glass seal material **36** which is likewise rammed to form the upper seal **36**. A terminal screw **30** is then positioned within the bore and the whole assembly is then heated to a temperature which softens the glass and chars the charrable, carbonaceous material, a temperature of 1550 to 1750° being generally satisfactory. A temperature of 1675° with an 18 minutes heating cycle and a 6 to 8 minute hold at the aforementioned temperature is preferred with the barium borate glass used in the preferred embodiment. Other temperatures may be employed for glasses which soften at a lower temperature. When the glass is sufficiently softened, pressure is applied to the terminal screw **30** to force it down into the centerbore, thereby depressing the softened materials and causing the upper seal portion **36** to surround and grip the lower end of the terminal screw. By hot pressing in this manner, which is the customary manner in the art, a continuous electrical path is formed from the terminal screw **30** to the center electrode head **28** through the resistance element and the conductive seal, the portions intermediate the top of the electrode and the bottom of the screw being sealed in glass-tight relationship with the walls of the insulator of the metal parts. The thus formed insulator assembly is then assembled in the shell **12** to form plug **10**.

EXAMPLE NO. 1

A resistor plug having a resistor seal composition containing 10.0 weight percent zinc, 26.7 weight percent glass, 43.6 weight percent zirconia, 16.7 weight percent Indian kyanite, 1.6 weight percent Thermax (carbon black), 0.4 weight percent dextrin and 1.0 weight percent borax was made by positioning the resistor composition about the center electrode head in the spark plug centerbore, placing a conventional conductive glass seal on top of the resistor composition and by pressing the terminal screw in to the resistor composition at a temperature in the range of 1500 to 1600° F. The resultant resistor spark plug was cut in half to observe the adherence of the resistor seal to the center electrode. The resistor composition adhered tightly to a zinc or a zinc-nickel coating which covered the nickel center electrode head. The good adherence was attributed to the formation of the metal coating on the center electrode head.

EXAMPLE NO. 2

A resistor spark plug having a resistor seal composition containing 10.0 weight percent antimony, 26.7 weight percent glass, 43.6 weight percent zirconia, 16.7 weight percent Indian kyanite, 1.6 weight percent Thermax (carbon black), 0.4 weight percent dextrin and 1.0 weight percent borax was made as described in Example No. 1. The resultant spark plug was cut in half to observe the adherence of the resistor seal to the center electrode. The resistor composition adhered tightly to an antimony or antimony-nickel coating which covered the nickel center electrode head. The good adherence was attributed to the formation of the metal coating on the center electrode head.

EXAMPLE NO. 3

A resistor spark plug having a resistor composition containing 7.0 weight percent tellurium, 26.7 weight percent glass, 43.6 weight percent zirconia, 16.7 weight percent Indian kyanite, 1.6 weight percent Thermax (carbon black), 0.4 weight percent dextrin and 1.0 weight percent borax was made as described in Example No. 1. The resultant resistor spark plug was cut in half and it was observed that the resistor composition adhered tightly to a tellurium or a tellurium-nickel coating which covered the nickel center electrode head.

The semiconductor materials that may be used in this spark plug resistor seal are of the type described in the patent to Counts et al., No. 3,235,655 granted Feb. 15, 1966, which describes a semiconductor material formed from the binary metal oxide systems consisting of TiO_2-ZrO_2, Ta_2O_5-ThO_2, Ta_2O_5-CeO_2 and Ta_2O_5-Di_2O_4 as well as the semiconductors described in the patent to Counts et al., No. 2,864,884 granted Dec. 16, 1958, where the semiconductor material comprises titanium oxide, tin oxide, tantalum oxide, vanadium oxide, molybdenum oxide, and tungsten oxide. The concentration of the semiconductor material is from 0 to 80 weight percent. An example showing the good adherence between this type of resistor composition when it contains zinc is given below.

EXAMPLE NO. 4

A resistor composition containing 5 parts by weight zinc, 33 parts barium borate glass, 23 parts kyanite, 2.4 parts thermax (carbon), 2.4 parts aluminum powder, 2.8 parts bentonite and 37 parts of a stannous titanate semiconductor consisting of 44.4 weight percent titanium dioxide, 29.6 weight percent alumina, 14.8 weight percent tin oxide, 7.4 weight percent tantalum oxide and 3.7 weight percent molybdic acid was prepared and placed in the spark plug insulator centerbore around the nickel center electrode head. After the resistor spark plug was completely assembled by the same steps as previously described, the resistor spark plug was cut in half to observe the adherence of the resistor to the center electrode. This resistor spark plug had a zinc-nickel alloy coating on the center electrode head and there was good adherence between the resistor composition and the center electrode head.

These examples indicate that the metals in the group consisting of zinc, antimony and tellurium promote the formation of a metal coating on the center electrode head which results in good adherence between the resistor composition and the center electrode head.

The resistor compositions of this invention contain a metal taken from the group consisting of zinc, antimony and tellurium which enable a good bond to be formed between the resistor seal and the center electrode thereby reducing the need of a conductor glass phase about the center electrode head. The resistor spark plug of this invention has a high degree of stability when subjected to field use since good contact between the center electrode head and the resistor seal is maintained for substantially the life of the resistor spark plug.

While the invention has been described in terms of specific examples, it is to be understood that the scope of the invention is not limited thereto except as defined by the following claims.

What is claimed is:

1. A gas sealing resistance composition for use in a resistor spark plug consisting essentially of glass having a softening temperature of from 1500–1750° F., an inert filler material in the amount of at least 15% by weight and a single metal powder taken from the group of relatively low melting point metals consisting of zinc, antimony and tellurium.

2. A resistance composition as described in claim **1** wherein the concentration of said metal powder taken from the group consisting of zinc and antimony is about 2 to 15 weight percent.

3. A resistance composition as described in claim 1 wherein the concentration of said tellurium powder is about 0.5 to 10.0 weight percent.

4. A gas sealing resistance element having a tight bond with the center electrode head in a spark plug insulator centerbore, said head having a coating of relatively low melting point metal deposited thereon from the gas sealing resistance composition, formed from a composition consisting essentially of 20 to 75 weight percent glass having a softening temperature of from 1500–1750° F., 15 to 80 weight percent inert filler, 0 to 60 weight percent semiconductor material, 0.1 to 4.0 weight percent carbon black, 0 to 3 weight percent inorganic binder, 0.1 to 4.0 weight percent water soluble charable carboneaceous material and 2 to 15 weight percent of a metal powder taken from the group of relatively low melting point metals consisting of zinc and antimony, said composition having been heated in said insulator centerbore to a temperature of from 1500–1750° F. at which said metal melts a portion of said metal forming a coating on said center electrode head.

5. A resistor spark plug comprising a ceramic insulator having a centerbore therethrough, a center electrode having its head in said centerbore and a fused gas sealing resistor mass bonded to said center electrode head, said head having a coating of relatively low melting point metal deposited thereon from the gas sealing resistor composition, said resistor mass consisting essentially of glass having a softening temperature of from 1500–1750° F., an inert filler material in the amount of at least 15% by weight and a metal taken from the group of relatively

low melting point metals consisting of zinc, antimony and tellurium, a portion of said metal forming a coating on the end of said electrode bonded to said resistor mass.

6. A gas sealing resistance element having a tight bond with the center electrode head in a spark plug insulator centerbore, said head having a coating of relatively low melting point metal deposited thereon from the gas sealing resistance composition, formed from the composition consisting essentially of 20 to 40 weight percent glass having a softening temperature of from 1500–1750° F., 50 to 70 weight percent inert filler, 1 to 3 weight percent carbon black, 1 to 3 weight percent inorganic binder, 0.2 to 3 weight percent water soluble charable carbonaceous material and 5 to 10 weight percent zinc powder having a relatively low melting point, said composition having been heated in said insulator centerbore to a temperature of from 1500–1750° F. at which said zinc powder melts, a portion of said zinc forming a coating on said center electrode head.

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