

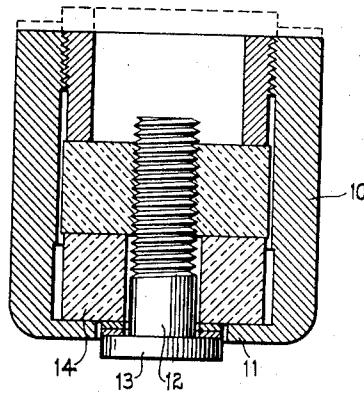
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SPARK GAP SEMI-CONDUCTOR

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SPARK GAP SEMI-CONDUCTOR

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This invention relates to ceramics and particularly to the particular type of ceramic which is employed in spark plugs as a semi-conductor for ionizing the spark gap. This is an improvement over the invention of White application Serial No. 248,845, filed September 28, 1951, now U. S. Patent No. 2,806,005, and is a continuation-in-part of application Serial No. 248,844, filed September 28, 1951, now abandoned.

There has recently been described in Patent No. 2,786,158, for instance, a new type of spark plug having a circular center electrode and a circumscribing electrode spaced therefrom which produces ignition by a flash across the gap between the electrodes and in which this flash is induced by a ceramic semi-conductor which overlies the gap. This construction is shown in the accompanying drawing wherein the outer barrel 10 of a spark plug terminates in an electrode 11 which is circular. Within this electrode 11, and spaced therefrom, is a center electrode 12 which is possessed of a circular head 13 which is spaced from the electrode 11 by a distance adequate to a good spark. Overlying the gap between the electrodes 11 and 13 is a ceramic semi-conductor 14 which operates to initiate the spark, theoretically by ionizing the air, or the gas, which is found between the two electrodes. In this way the spark is caused at lower tension than was possible with plugs of prior art type.

These new spark plugs have introduced an improvement in the operation of motors, but they have also introduced problems which never existed before. It is an object of this invention to recognize and to correct the problems which exist in these new spark plugs.

The words "semi-conductor" or "spark gap semi-conductor" will be employed in this specification and in the claims to describe the piece of semi-conductive ceramic which is employed to bridge the gap. Some semi-conductors have been used heretofore, but they have been accompanied by difficulties in operation or in construction. For example, it has been difficult to obtain a spark gap semi-conductor of a proper conductivity, which will also have those characteristics of durability and resistance to conditions existing within engines, which is essential to satisfactory life. It is important that the spark gap semi-conductor shall have excellent resistance to erosion under the conditions of sparking and of ignition which exist in modern engines, but this has been difficult to obtain with known ceramics. Furthermore, it has been necessary to find ceramics which are capable not only of withstanding the high temperatures which exist within an engine during the time of ignition of the charge, but the great variation in temperatures which exists between the time of firing and the time of discharge and admittance of the cold charge. Therefore, it is not only necessary that these resistors have proper conductivity, proper resistance to erosion, but that they have proper resistance to heat and to rapid changes in temperature. Furthermore, it is necessary that these spark gap semi-conductors shall have the strength to withstand high pressures, not only gaseous but also mechanical and that, being some-

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what porous, they may withstand internal high pressures as well as compressive pressures without disruption. It is necessary that they shall have excellent resistance to thermal shock, which arises by reason of repeated rapid changes in temperature. It is also desirable that the porosity of the pieces shall be low in order that the pressures existing on the outside of the piece may not enter within it and act disruptively. Furthermore, it is necessary that the porosity be low in order that the piece shall not act as an accumulator of carbon which, being a good conductor, is able by presence in sufficient amount to change the conductivity of the semi-conductor and, consequently, its operating characteristics within the engine.

The applicant has had great experience with all the semi-conductors employed in the prior art and has found that they have material failings in one or all of the categories hereinabove discussed. It is consequently an object of the invention to make a dense, relatively non-porous semi-conductor of proper conductivity, of good resistance to erosion, to high temperature, of strength to withstand high pressures, both gaseous and mechanical, and of good resistance to thermal shock. The objects of the invention are accomplished generally speaking by a ceramic spark gap semi-conductor having as its essential ingredients a major proportion of silicon carbide and a minor proportion of tricalcium penta aluminate, and also some cobalt oxide, alumina and silica.

The silicon carbide employed is preferably of fine grade. A silicon carbide which has been satisfactorily employed has analyzed free carbon about .5%, silicon dioxide about 1.4%, iron oxide about .5%, aluminum oxide about 1% and silicon carbide about 96%. This silicon carbide should be of a particle size such that a minimum of 98% passes through a sieve having a minimum of 325 mesh, which means holes per square inch. In general, it is preferred that the silicon carbide shall pass through a 400 mesh sieve. This is used in an amount constituting about 40-86% of the ceramic ingredients.

The second material employed in the ceramic mixture is cobalt oxide, preferably black cobalt oxide analyzing a minimum of 70% cobalt and of a particle size such that a minimum of about 90% passes through a 325 mesh sieve. This is used in an amount constituting about 5-40% of the ceramic ingredients. Cobalt oxide may be replaced with equivalent amounts of the oxides of the iron period, particularly manganese, nickel, cobalt and iron. Molybdenum oxide of the silver period is also useful. An excess of this ingredient should be avoided, as it separates out and runs off during firing. Optimum electrical properties are attained with cobalt oxide present at about 20%. In order to avoid impairment of electrical properties, the amount of this ingredient should not fall materially below 5% although as little as 4% black cobalt oxide has been used.

The third ingredient of the new ceramic contains alumina, which preferably is of high grade, tricalcium penta aluminate ($3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$) and some silica, this mixture being present in the range 10-40% by weight of the ceramic ingredients. The third ingredient may have a composition lying in the following range in percent by weight of the third ingredient:

Al_2O_3 -----	2-15.
$3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ -----	0.5-6.0.
SiO_2 -----	At least 80.

A typical third ingredient has ingredients having individual amounts on the order of 13% alumina, 1.5% tricalcium penta aluminate, and .3% silica, the last three percentages being based upon the total weight of all the material employed in the ceramic mixture. As an alternative mode of defining the composition of the third ingredient, the alumina, tricalcium penta aluminate, and

the silica thereof may be said to be present in the third ingredient in the ratios on the order of 13:1.5:3 by weight. These may be of medium particle size, a particle size capable of passing a screen of 200 mesh being adequate, but a finer particle size capable of passing a screen of 325 mesh is preferred. Particle sizes ranging from 180 to 600 mesh have been used at this stage of the process, but the indicated sizes are preferred.

The raw materials are mixed in the proportions stated, a specific composition silicon carbide 80%, cobalt oxide 5%, aluminum oxide 13.2%, tricalcium penta aluminate 1.5%, and silicon dioxide .3% being exemplary, and ball milled in water for 4 hours using about 2 parts distilled water for each 1.6 parts of ceramic. Ball milling may be extended or shortened depending upon the ingredients employed and the time necessary to reduce them to a state of suitable size and intermixture.

After the mixing has been satisfactorily completed, the slurry may be poured into a drying pan and the mill should be rinsed with a small amount of distilled water and the water added to the slurry. The drying pan is oven dried at 200–300° F. until the moisture content is less than 1% as determined by Dietert moisture determinator on 15 minute exposure. The slurry after drying is passed through a 100 mesh screen to remove lumps and mill particles.

The ceramic mix as thus prepared may be molded and fired, but molding is facilitated by incorporating into the mix a suitable binder of the type which has heretofore been employed in molding ceramics, for example, flour, urea formaldehyde resins, polyvinyl alcohol, and sulphite liquor, for instance, of the type called goulac. The binder is satisfactorily composed of about 30% of the weight of the ceramic mix, half of that weight being the binder itself, and half being water. When the binder is urea formaldehyde resin, about .5 part by weight will ordinarily prove sufficient. After thorough mixing with the binder the ceramic mix is partially dried at 200° plus or minus 10° F. in an oven for 15 to 20 minutes or until the material will granulate through a 20 mesh screen, after which it is oven dried for about a half hour at 200° plus or minus 10° F. or until the granules will flow freely with no tendency to cling together and the moisture content as determined by a Dietert computer, after 10 minutes exposure, is 1.2 to 2%.

The foregoing composition is molded in any of the ways which have heretofore been satisfactory for the molding of ceramic pieces, preferably dry under heavy pressure on the order of 30 to 40 thousand pounds per square inch. Drying of the molded piece is not essential, it can be fired immediately, for instance, in an electric kiln at a temperature sufficient to down Orton's pyrometric cone 19. A satisfactory firing schedule commences at 0 hour at room temperature, at 1 hour has obtained 1200 plus or minus 50° F., at 2 hours has obtained 1900 plus or minus 50° F., at 3 hours has obtained 2400 plus or minus 50° F. and at 4 hours (plus or minus 1/4 hour) cone 19 is down, which indicates approximately 2780° F. The cone is considered down when the tip touches the plaque. In general the peak temperature should not exceed cone 20 at 3 o'clock. The kiln preferably admits air during firing or is supplied with a gas comprising oxygen. It is not altogether certain what takes place during firing, but a present theory postulates a partial oxidation of the SiC and a partial reduction of the cobalt oxide, leading to an increased conductivity of the piece, but the applicant is not to be bound by the theory.

After cooling, the piece may be machined as desired, then may be washed in distilled water, and dried to con-

stant weight in a 200° F. oven. This sometimes requires four hours or more of drying.

The semi-conductors which are made according to this process are believed to be excellent in all respects and are particularly superior in strength. They have a resistance within the best range of semi-conductivity; they resist erosion better than prior art semi-conductors; they resist spark erosion and their resistance to heat and high temperature is very good; they have superior strength to withstand both mechanical and gaseous high pressures; they resist the thermal shock which comes from rapid changes in temperature accompanied by rapid changes in pressure; they have low porosity and they do not absorb sufficient carbon to materially alter their performance characteristics during use. They are inert at operating temperature and do not form deposits on the electrodes.

Although only a limited number of embodiments and modifications of the invention have been illustrated in the drawing and mentioned or described in the foregoing specification, it is to be expressly understood that the invention is not limited thereto.

What is claimed is:

1. A spark gap semi-conductor consisting essentially of 40–86% silicon carbide, 4–40% of one of the group consisting of cobalt oxide, manganese oxide, and molybdenum oxide, and 10–40% of a mixture consisting essentially of a major part of alumina, a minor part of $3\text{CaO}-5\text{Al}_2\text{O}_3$, and a trace of silica, the alumina, $3\text{CaO}-5\text{Al}_2\text{O}_3$, and silica having a weight ratio with respect to each other of about 13:1.5:3.

2. A spark gap semi-conductor having the composition silicon carbide about 80%, cobalt oxide about 5%, alumina about 13.2%, tricalcium penta aluminate about 1.5%, and silica about 0.3%.

3. A spark gap semi-conductor consisting of 40–86% silicon carbide analyzing about 96% SiC, 4–40% of one of the group consisting of cobalt oxide, manganese oxide and molybdenum oxide, and 10–40% of a mixture consisting essentially of a major part of alumina, a minor part of $3\text{CaO}-5\text{Al}_2\text{O}_3$, and a trace of silica, the alumina, $3\text{CaO}-5\text{Al}_2\text{O}_3$, and silica having a weight ratio with respect to each other of about 13:1.5:3.

4. A spark gap semi-conductor consisting essentially of 40–86% silicon carbide, 4–40% of one of the group consisting of cobalt oxide, manganese oxide, and molybdenum oxide, and 10–40% of a mixture consisting essentially of a major part of alumina, a minor part of $3\text{CaO}-5\text{Al}_2\text{O}_3$, and a trace of silica, the alumina, $3\text{CaO}-5\text{Al}_2\text{O}_3$, and silica in the mixture respectively lying within the following ranges in percent by weight of the said mixture: at least 80%, from about 2 to about 15%, and from about 0.5 to about 6.0%.

5. A spark gap semi-conductor consisting of 40–86% silicon carbide analyzing about 96% SiC, 4–40% of one of the group consisting of cobalt oxide, manganese oxide and molybdenum oxide, and 10–40% of a mixture consisting essentially of a major part of alumina, a minor part of $3\text{CaO}-5\text{Al}_2\text{O}_3$, and a trace of silica, the alumina, $3\text{CaO}-5\text{Al}_2\text{O}_3$, and silica in the mixture respectively lying within the following ranges in percent by weight of the said mixture: at least 80%, from about 2 to about 15%, and from about 0.5 to about 6.0%.

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