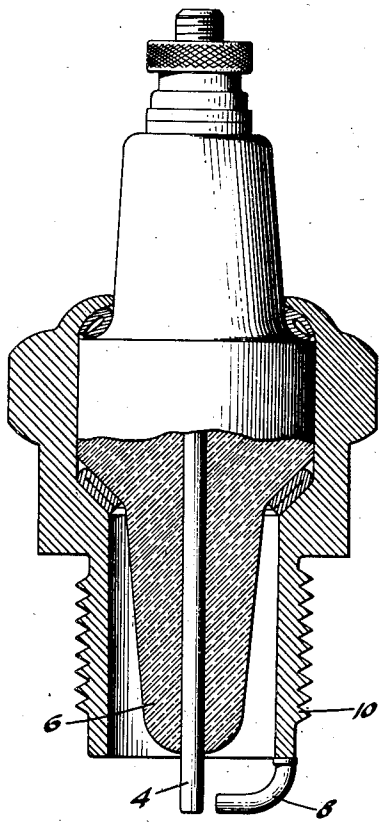
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SPARK PLUG ELECTRODE AND OTHER ELECTRON EMITTING DEVICES

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SPARK PLUG ELECTRODE AND OTHER ELECTRON EMITTING DEVICE

Application filed March 2, 1931, Serial No. 519,652, and in Great Britain October 11, 1928.

This is a continuation in part of our application Serial Number 302,904, filed August 30, 1928.

Spark plugs, such as are commonly used upon internal combustion engines, consist essentially of a pair of electrically conducting elements separated by an insulator. The ends of these elements called electrodes, are spaced in such a way as to provide a gap across which the electric spark is caused to jump to ignite the combustible mixture.

One of the principal difficulties encountered with spark plugs is the fact that the coating produced by the combustion gases over the exposed part of the plug may, in time, interfere with the ignition. The coating consists of various by-products of combustion, such as carbon, iron oxide, and the like, as well as special compounds sometimes formed where anti-knock fuels are employed. The coating increases as the spark plug is used and, as it is a relatively good conductor of electricity, in time provides a conducting path parallel to the path across the gap, of sufficiently high conductance so that the current flows through this coating instead of jumping the gap between the electrodes. The result is that the engine misses,—that is, some cylinder fails to give power impulses because no spark is delivered at the gap to ignite the combustible mixture.

In the present day ignition equipment a spark coil or magneto supplies the sparking voltage. The design of this equipment is necessarily such that the available voltage falls off abruptly with increase in the conductance along the path constituted by the coating on the insulator. After the initial sharp reduction, the voltage drops more gradually with increase in the conductance along the said path. As a result of this characteristic of the ignition apparatus, it is apparent that a plug requiring a high sparking voltage will become fouled very much more quickly than a plug requiring a low sparking voltage. In the case of one typical ignition system, in a test in which plugs were operated under identical conditions, it was found that while a plug having a sparking voltage of 8,000 volts ceased to fire the combustible mixture of the engine when enough coating had collected on the insulator to form a leakage path of 1.5 micromhos, a plug having a sparking voltage of 4,000 continued to operate until the leakage path reached a value of 10 micromhos. Since it would take several times as long for enough to collect on a plug to increase the conductance of the leakage path to 10 micromhos as it does to reach a value of 1.5 micromhos, the plug operating at the lower voltage will give satisfactory service for a far longer period of time than the other. The importance of operating the plug at low voltages is clearly apparent.

It has been known, heretofore, that the sparking voltage varies with the length of the gap and the density of the gases in the combustion chamber at the instant of ignition, and with the temperature of the electrodes. It was also known that the sparking voltage varies with the shape of the electrodes but it has heretofore been universally accepted that the sparking voltage was practically independent of the materials employed in the composition of the electrodes. However, upon testing a large number of spark plugs of identical construction under the same conditions of gap width, gas density, and electrode temperature, we noted considerable variation in the sparking voltage that could not be satisfactorily explained.

We also knew, from past experience, that the voltage required to cause a spark to pass between electrodes of a spark plug gradually increases with time and use, and eventually becomes higher than the maximum that the ignition coil will generate. This effect is exaggerated under cold weather starting conditions. No satisfactory explanation of either of the above phenomena was advanced but it remained the fact that apparently identical plugs, operated under identical conditions, would spark at widely varying voltages and that the same plug, operated under apparently the same conditions, would require higher voltages to produce the spark as time went on.

The materials, usually metals, of which spark plug electrodes have always been made are of commercial purity. The electrode

metal is usually an alloy made in accordance with a definite formula and, upon chemical analysis, shows the presence of the chosen ingredients only. However, it occurred to us that possibly the wide variations in sparking voltages in apparently identical plugs and in the same plug after a period of use were due to the presence in the electrodes of impurities, widely varying in amount, but always in such minute traces as to escape detection by ordinary chemical analysis. Accordingly a thorough laboratory investigation was made to determine what, if any, change took place in the composition of the electrode wire with changes in the sparking voltage. With the aid of thermionic studies under vacuum and of spectrum analysis it was found that the spark plug electrode alloy consisting of approximately 98% nickel and 2% manganese, contained traces of a number of other elements, and among them frequently magnesium; that under conditions of use the magnesium left the alloy at a greater rate than the nickel and as the supply of magnesium in the alloy became depleted the sparking voltage rose. To check this conclusion spark plugs were made having electrodes from which all traces of magnesium had been removed by long continued heating in vacuum. Tests of these plugs in all cases showed much higher sparking voltages. Spark plugs were also made having electrodes containing appreciable percentages of magnesium as contrasted with the microscopic traces often occurring in the commercial alloy. Upon testing, these plugs showed markedly lower sparking voltages, but the voltage varied considerably not only from spark to spark but even more markedly at points erratically spaced along the length of the electrode. These variations we found to be due to the fact that magnesium was present in the wire as small irregularly spaced inclusions and did not form a true solution or alloy with the nickel. In further confirmation of the accuracy of our conclusions, we found that as the magnesium was evaporated, or otherwise removed from the electrodes, the sparking voltage rises. This explains the rising of the sparking voltage with continued use of the plug. Furthermore, plugs which failed to spark in actual use in an engine were found to have electrodes (of the usual alloy) deficient in magnesium or entirely lacking that element. Because of these undesirable variations in voltage with alloys containing magnesium we were led to search for materials that would better serve our purpose.

After exhaustive research and thorough study of the problem we have found that there is a definite class of elements that, from theoretical considerations, should, when employed in spark plug electrodes, markedly reduce the sparking voltages. These elements are characterized by a low work function. By "work function" is meant the amount of work necessary to remove an electron from the element. Work function may be measured by measuring the thermionic emission and in various other ways. The elements of low work function are also, in general, characterized by the fact that they are strongly electropositive, and include the alkali and alkaline earth metals. The group of elements having low work function comprises lithium, sodium, potassium, rhubidium, cæsium, beryllium, magnesium, calcium, strontium, barium, thorium and radium.

Aside from low work function, however, there are other factors which determine the usefulness of elements in spark plug electrode work. Thus they should be capable of being easily alloyed with, or uniformly distributed throughout the other elements, such as nickel and/or manganese, which it is desirable to include in the alloy from the point of view of electrical conductivity and resistance to heat and corrosion. It is also important that the added elements shall not be readily removed from the base material. In other words, it is important that the rate of depletion of the element or elements of low work function from the alloy shall be low. This insures that the plug will operate for long periods of time at the desired low voltage.

Our researches to date indicate that of the above group the only ones that are capable of practical use in spark plug electrodes are the alkaline earth metals, barium, calcium and strontium. The alkali metals have proven to be impracticable because, in the first place, owing to their rapid oxidation, it was practically impossible to include enough of the alkali material in the mixture to be of any value and, in the second place, the small amount that was included evaporates from the wire at so great a rate under conditions of use as to have but a temporary effect on the sparking voltage. Thus, a nickel alloy containing traces of sodium was tested by heating a wire made of the material. At the end of an hour's heating, no traces of sodium could be detected even spectroscopically. Further tests of such alloys in spark plugs showed such an increase in sparking voltage after but a few thousand sparks that it was evident that practically all the sodium had disappeared from the wire.

The alkaline earth metals, barium, calcium and strontium, when included as an integral part of the spark plug electrode, markedly reduce the sparking voltage, and the electrodes retain this property over a long period of time. We have previously pointed out the lack of uniformity in sparking voltage that characterizes the nickel magnesium alloy. This is objectionable because ignition is thereby rendered irregular, and as time goes on, the sparking voltage rises and the engine be-

comes harder to start. Nickel wire having strontium intimately distributed throughout it, has much the same characteristics as the nickel magnesium wire. The strontium and nickel do not form a solid solution or alloy, the strontium occurring as inclusions throughout the wire. While the sparking voltage is reduced by the presence of strontium, there is considerable lack of uniformity in the sparking voltage.

Barium and calcium, on the other hand, alloy well with nickel, forming true solid solutions. As a consequence the sparking voltage remains uniform. From experiments we have made, however, we are led to believe that of the two the barium alloy is much to be preferred for its rate of evaporation from the alloy is much less, so that the barium not only gives a large reduction in sparking voltage but maintains that property almost indefinitely.

When any of the alkaline earth elements, calcium, strontium or barium, is included in a spark plug electrode composition, in an amount even as low as one one-hundredth of one per cent, a large and more or less permanent reduction in sparking voltage will result, amounting to as much as 25% in the case of barium; and, at the same time, the variation in voltage between successive sparks is greatly reduced. In practice we prefer to use larger amounts of the low work function material in order to secure a greater reduction in sparking voltage, the upper limit of the amount used being usually determined by considerations of convenience in manufacture and cost.

We believe that the results obtained by the use of these materials in spark plugs may be explained by the electron theory of the conduction of electricity through gases. This theory sets forth that in order to produce a spark, there must be built up between the electrodes a continuous flow of electrons. In order to initiate this flow, there is required in the gap the presence of a number of free ions. Such free ions are always found in gases in containers and in the free air. These are accelerated by the electric field and in traveling toward the electrodes collide with gas molecules at such a rate as to form other free ions by the impact of their collision. Furthermore, the positive ions colliding with the cathode, or negative electrode, cause the removal therefrom of electrons which pass through the gas to the anode. These electrons in passing through the gas make collisions with gas molecules and form free ions and electrons by the violence of their impacts. On account of their relatively high mobility with respect to free ions, the electrons constitute the principal carriers of electric charges through the gas between the electrodes. The amount of the current depends principally upon the number of electrons that can be made to pass per second through the gas and the rate of building up of the current depends largely upon the number of electrons that can be removed from the cathode per second. Besides the action of the collisions of positive ions upon the cathode, other processes are operative to remove electrons from the negative electrode, viz: the photoelectric action of light generated in the gap between the electrodes by the passage of electric charges or of light from sources external to the spark gap, the thermionic emission of electrons from the cathode as a consequence of its being heated by surrounding bodies or by the heat generated by the positive ions impinging upon it, and the action of the electric field in extracting electrons from the cathode. In each of these processes energy must be expended in extracting the electrons in proportion to the work function of the material of the electrode, and the number of electrons that can be removed per second will be increased by the inclusion in the material of the electrode of substances of low work function, because of the relative ease with which the electrons are extracted from the mass. If the rate of removal of electrons is decreased the rapidly rising ignition coil voltage will build to a higher value before the necessary electrons are available for the conduction of sufficient current to limit the rise of voltage. The inclusion in the material of the electrodes of substances of low work function will reduce the sparking voltage because of the increase in the rate of extraction of electrons from the cathode and the consequent increase in the rate of rise of current under the combined action of such of the processes mentioned above as are operative at any given instant. The differences in rate of thermionic emission of the materials which occur in the electrode either in microscopic traces or in appreciable quantities explains the mysterious variations in "time lag" of the spark that have heretofore been a subject of much conjecture.

While the above is the best explanation of the theory of the operation of these elements according to present day knowledge, it is to be emphasized that the precise character of the phenomenon called the electric spark is not known, and the above statement is to be considered in the light of a tentative explanation and not in the nature of a limitation of this invention.

It is obvious that the above elements will function to produce the desired result when included in electrodes of widely varying composition; thus, our invention is applicable with electrodes composed of other base metals, such as copper, or of non-metals. However, in general other base materials are not as satisfactory as nickel, either because of lack of resistance to corrosion or oxidation, or prohibitive cost. It is likewise apparent that our invention is applicable to spark plugs of

whatever design, and, in general, to sparking or ignition devices operating under similar conditions. In this field we believe our invention to be of pioneer character, for heretofore it had not been recognized that the electrode material had any practical effect on sparking voltage.

In the drawing is illustrated a conventional spark plug provided with electrodes made in accordance with this invention.

In the figure, we have shown a spark plug including a center electrode 4, surrounded by insulator 6 of the usual ceramic composition, while the insulator, in turn, is surrounded by the steel shell 10, carrying the electrode 8. Either or preferably both of the electrodes 8 and 10 are made of an alloy or composition including a proportion of one or more of the alkaline earth elements above mentioned. As previously pointed out, this proportion may be as low as .01%, but as it is desirable to obtain a greater reduction in sparking voltage a somewhat larger percentage should be used. The remainder of the composition preferably consists principally of nickel.

A preferred composition of alloy for spark plug electrodes which has given excellent results both from the standpoint of low sparking voltage and uniformity in sparking voltage is given below:

	Per cent
Manganese	1.8
Barium	.03
Magnesium a trace	
Balance nickel	

The amount of magnesium present in the alloy is so small, so difficult to measure by ordinary methods of chemical analysis, and so non-uniformly distributed that it has been designated as a trace. It is the residue of about .1% magnesium added to de-oxidize the alloy and increase its ductility so as to permit easy drawing.

A barium content of .03% has been chosen for spark plug use because the addition of more barium, while reducing the sparking voltage, does not reduce it by an additional amount sufficient to warrant the expense. A barium content as low as .01% will, however, effect an appreciable lowering of the sparking voltage.

A manganese content around 1.8% will be found adequate for spark plug uses but there may be considerable variation in the percentages of both this ingredient and of nickel.

Spark plugs having electrodes made of the above alloy have, upon test, shown sparking voltages 25% lower than the average voltages obtainable with electrodes of the usual nickel-manganese alloy, and whereas with the latter material the sparking voltage varied as between successive sparks, when operated under the same conditions, by 1,000 to as much as 4,000 volts, with our improved electrodes the variation in voltage as between successive sparks does not exceed 400 or 500 volts. With the barium alloy, the plug retains these characteristics throughout substantially its entire life for the barium evaporates from the electrode at a rate but little greater than that of the nickel.

We have also found that the barium increases the resistance of the electrodes to corrosion, actual tests show an increase in electrode life of 25%.

In preparing the alloy the barium, which is readily oxidized, is sealed within a can made of ordinary tin plate, or is wrapped in nickel foil and the package is immersed in the molten nickel-manganese alloy. The foil or the can melt and mix with the other ingredients but the amount of foreign material thus introduced is so slight as to have practically no measurable effect on the alloy. The advantage of this method of preparing the alloy is that the barium is kept out of contact with the air and becomes alloyed with the nickel and manganese before it has opportunity to oxidize. Owing to the volatility of the barium, it is desirable that the temperature of the melt should be but little above the melting point of nickel at the time it is introduced and after introduction the melt should be allowed to stand before casting only long enough to insure complete alloying. However, to secure the maximum barium content such as is needed in vacuum tubes and the like, and to insure the least waste of barium, it is best to employ the method of procedure described and claimed in the co-pending application of D. W. Randolph Serial No. 520,704 filed March 6, 1931. By the above described methods of preparation we have found that the barium is uniformly distributed throughout, forming a true solid solution or alloy.

The proportions given above are, as previously stated, not critical. The percentages of the ingredients have, for example, been varied within the following range:

	Per cent
Manganese	.5 to 10
Barium	.01 to .20
Magnesium a trace	
Balance nickel	

We have so far succeeded at times in producing by the processes herein referred to alloys containing as much as .15% barium, although most of the time not more than .04% barium was achieved. By the improved method claimed in the Randolph application alloys have consistently been made containing .17% barium, and at times as much as .20% barium has been included. It is expected that by improvements in furnace technique now being experimented with, larger percentages of barium may be obtained.

Instead of using nickel as the base metal we may use cobalt, an element of well recognized similar characteristics. Cobalt will not

be as satisfactory, however, for spark plug work, where corrosion is a factor, for it has relatively poor corrosion resisting properties. Elsewhere its use may be desirable. In the broader claims we have grouped nickel and cobalt together under the term "nickel-cobalt" metal.

We have also made and tested alloys of barium with copper, with silicon and with chromium as base metals. The copper-barium alloy is not as resistant to corrosion as is desirable for spark plug work. The same is true of the silicon-barium alloy. The barium-chromium alloy has proven to be unworkable by ordinary drawing methods because of its extreme hardness and lack of ductility. More recent tests have indicated that the rate of emission obtained from alloys having copper, silicon or chromium as a base is so low compared with nickel or cobalt as to render them undesirable from a practical standpoint. Silicon particularly seems to retard emission.

We have also had success with calcium-nickel alloys. While calcium does not seem to reduce the sparking voltage as much as barium and also evaporates from the electrode more rapidly than barium, it is, nevertheless, next to barium in desirable qualities. Calcium may be alloyed with nickel or with nickel and manganese just as in the case of barium. The alloy is prepared in the same manner as the barium alloy. We have found the following composition to be effective for spark plug electrodes:

	Per cent
Calcium	.04
Manganese	2.00
Magnesium	a trace
Balance nickel	

There is nothing critical about the proportions of the ingredients except that the calcium should be in excess of .04% of the total to insure that it will have sufficient effect in reducing the sparking voltage. In actual practice the quantity of calcium used will be in excess of this amount. We have used up to .10% calcium. In general the reduction in sparking voltage will increase in proportion to the amount of the low work function element that is added but it is undesirable to increase the calcium content unnecessarily for reasons of economy.

As in the case of barium, calcium may be employed with base metals other than nickel, for example, cobalt, copper, silicon or chromium. These base metals, however, have the objections pointed out in connection with barium.

Strontium may be combined with nickel in the same manner. However, we have been unable to produce true alloys and owing to the uneven distribution of this metal in the wire we have not obtained uniformity in sparking voltage, and owing to the fact that the metal evaporates from the wire much more rapidly than the other, the continued use of electrodes containing it is accompanied by increase in sparking voltage due to depletion of the electron emitting substances.

Many modifications will occur to those skilled in the art, for example, it may prove desirable to employ two or more electron emitting elements instead of one in the alloy. The barium alloys herein disclosed are claimed in our copending application, Serial No. 574,050, filed November 9, 1931.

We claim:

1. A spark plug having an electrode having interspersed throughout its cross section a material of low work function for reducing the sparking voltage.

2. A spark plug having an electrode having interspersed throughout its cross section an alkaline earth material of low work function for reducing the sparking voltage.

3. A spark plug having an electrode comprising a base material resistant to heat and corrosion and a material of low work function distributed throughout the base material for reducing the sparking voltage.

4. A spark plug having an electrode formed of nickel-cobalt metal and an alkaline earth metal of low work function for reducing the sparking voltage.

5. A spark plug having an electrode formed of an intimate mixture of nickel-cobalt metal, manganese, and an alkaline earth metal of low work function for reducing the sparking voltage.

6. A spark plug having an electrode formed of an alloy of nickel and barium said barium having the property of low work function thereby reducing the sparking voltage.

7. A spark plug having an electrode formed of an alloy of nickel, manganese and barium said barium having the property of low work function thereby reducing the sparking voltage.

In testimony whereof we affix our signatures.

ORA S. DUFFENDACK.
HECTOR RABEZZANA.