

Feb. 17, 1942.

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2,273,704

ELECTRICAL CONDUCTING MATERIAL

Filed Oct. 10, 1935

2 Sheets-Sheet 1

FIG. 1

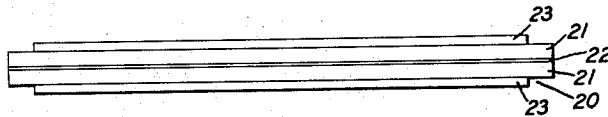


FIG. 2

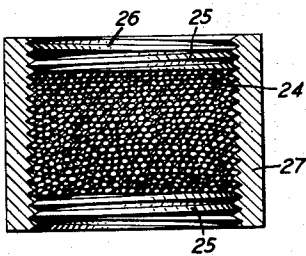


FIG. 3

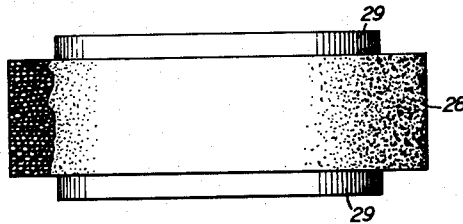


FIG. 5

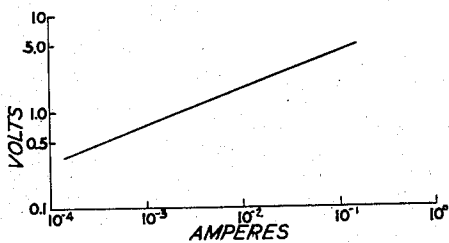


FIG. 6

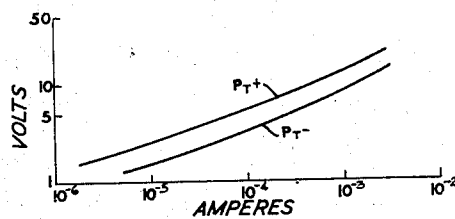


FIG. 4

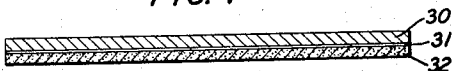


FIG. 8

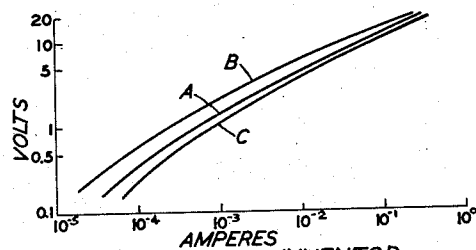
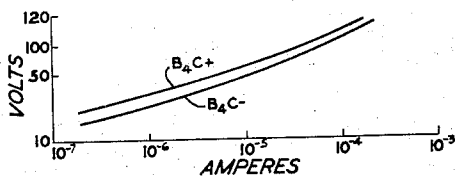


FIG. 7



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2 Sheets-Sheet 2

FIG. 9

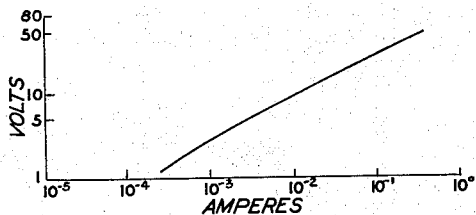


FIG. 10

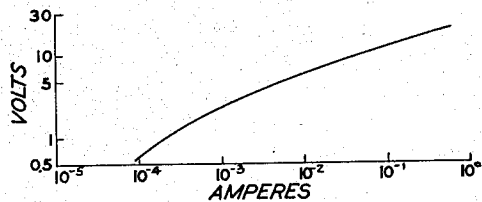


FIG. 11

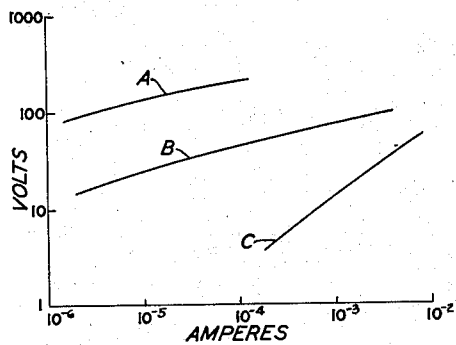


FIG. 13

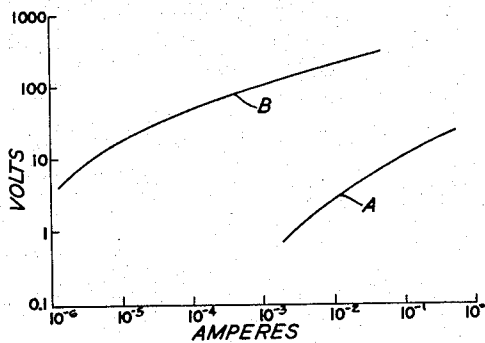


FIG. 12

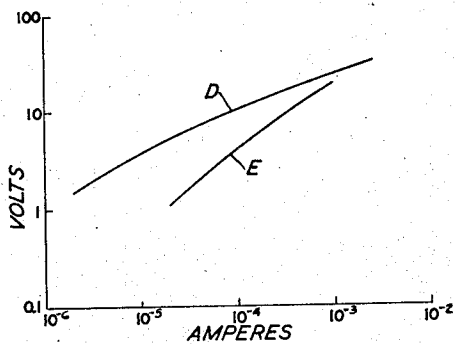
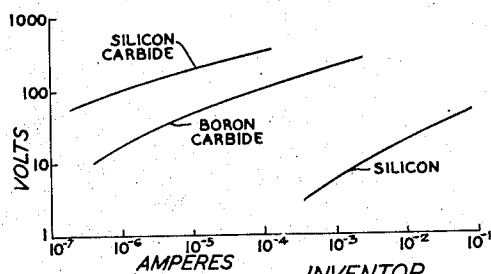


FIG. 14



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## UNITED STATES PATENT OFFICE

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## ELECTRICAL CONDUCTING MATERIAL

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Application October 10, 1935; Serial No. 44,344

15 Claims. (Cl. 201—72)

This invention relates to electrical conducting materials and, more particularly, to such conducting materials having a non-linear voltage-current characteristic.

An object of this invention is to improve the methods of manufacture and the characteristics of non-ohmic conducting materials.

Another object is to produce non-ohmic conducting materials having reproducible characteristics and undergoing no irreversible changes in normal use because of change in temperature or continued application of excess voltages.

Still another object is to produce conducting materials showing non-ohmic characteristics at potentials between a few hundredths of a volt and a few hundred volts.

A further object is to improve methods of depositing films of semi-conducting or insulating materials on metallic or semi-conducting plates, members or granules.

Other and further objects will be apparent from the detailed description which follows hereinafter.

In accordance with this invention, a non-ohmic conductor is provided by associating a pair of plates, discs or members of a metal or of a semi-conducting material separated by a thin film of an insulating material. If the separated members are of the same material, the non-ohmic characteristic is symmetrical; if the members are of different materials, the characteristic is asymmetrical. A non-ohmic conductor is obtainable, also, by coating individual granules of a conducting material with an insulating film and, thereafter, compressing or bonding them together, metallic contact being made to the surfaces of the unit thus formed. When a bond is employed, it is preferable that it should not react chemically with or tend to dissolve the compound of which the film is composed.

A more complete understanding of this invention will be obtained from the detailed description which follows taken in conjunction with the appended drawings, wherein:

Fig. 1 shows a non-ohmic conducting device embodying the invention;

Fig. 2 shows another embodiment of the invention in the form of a compressed granular aggregate;

Fig. 3 shows still another embodiment of the invention in the form of a compressed, bonded granular aggregate;

Fig. 4 shows another embodiment of the invention; and

Figs. 5 to 14 show characteristic curves of

various electrical conducting materials or devices in accordance with the invention.

Materials or devices whose conductivities increase as the potential applied to them increases, that is, materials in which the current increases more rapidly than linearly with voltage, are defined as non-ohmic conductors. If the conductivity is electronic, the conductor is called an electronic non-ohmic conductor. In general, the conductivities of electronic non-ohmic conductors are independent of the wave shape, of the frequency, and, except for efforts due to Joule heating, of the duration of application of the applied potential, being dependent only on the mean magnitude of this potential. There are, however, electronic non-ohmic conductors whose conductivities are functions of the polarity of the applied potential, such materials being referred to as asymmetric non-ohmic conductors. With the latter conductors, capable of rectifying alternating current, it is generally found that, while for a given polarity of applied potential, the conductivity is non-ohmic as above defined, the conductivity for a potential of opposite polarity may decrease over certain ranges as the potential is increased, that is, the current may increase less rapidly than linearly with applied potential.

It has been found that materials ordinarily regarded as insulators become conductors when used in thin films between two conducting bodies in such a way that the voltage gradient in them is great, and that, except in cases where measurements have been made near the point of dielectric breakdown, non-ohmic conduction is observed only at solid-solid interfaces, and that the so-called body or intrinsic conductivity of solids is strictly ohmic.

It has been usually assumed that non-ohmic conduction occurs only at interfaces between semi-conductors or between semi-conductors and metals, a semi-conductor being defined as a material whose conductivity is much less than that of a metal but much greater than that of an insulator. It has been found, however, that such an assumption is not correct, and that apparently the sole requirement for non-ohmic conduction is that the surfaces of two conducting bodies be separated by a physically thin film of a material possessing a low intrinsic specific conductivity. When, furthermore, bodies of the same intrinsic conductivity are separated by such a film, the arrangement exhibits symmetrical non-ohmic conductivity; when the film separates bodies of widely different conductivities, for example, a

metal and a semi-conductor, the conductivity will be asymmetric, the arrangement acting as a rectifier for applied alternating potentials.

While it has been observed that physically thin films of materials, such as adsorbed gases, waxes, oils and other organic substances forming interfacial layers between conducting bodies give rise to the effects mentioned hereinabove, such materials are in many cases too unstable to be employed in a non-ohmic conductor to be used in an electrical circuit. This invention, therefore, is directed to the production and utilization of thin films of inorganic materials, such as metallic oxides and silicates that are known to be stable. Both symmetric and asymmetric non-ohmic conductors have been produced from a variety of materials.

There are at least two distinct methods of producing symmetrical non-ohmic conductors. The first of these is the creation of a thin film of a material having a low specific conductivity as an interfacial layer between parallel surfaces of two bodies having the same specific conductivity. The second method is to coat granules of a conducting material with such thin films and then to compress an aggregate of such film-coated granules between a pair of metallic electrodes, or to bond such granules in a matrix which holds them in contact, metallic contact being made to the surfaces of the bonded aggregate. It can be shown statistically that when granular aggregates are employed, it is not necessary that the specific conductivity of each granule be the same as that of every other one, since, if the size of the granules be small compared to the dimensions of the aggregate, the probability that there are an equal number of contacts exhibiting asymmetric conductivity in either sense is unity. Thus, while symmetric non-ohmic conductivity can be obtained by combining large numbers of asymmetric non-ohmic conductors in a random manner, asymmetric non-ohmic conductivity can arise only when there is but one interface or when all interfaces are present in an ordered system.

Fig. 1 shows a symmetric non-ohmic conductor or device, designated generally 20, comprising a pair of layers or plates 21, 21 of a semi-conductor, such as boron carbide or silicon carbide separated by a thin film 22 of an insulating or other material of low specific conductivity, such as lead oxide, the outer surfaces of the layers 21 being engaged by metallic contacts 23, 23, applied thereto, for instance, by spraying. The contacts 23 may be omitted if a suitable metal is substituted for the semi-conductor layers. Such a metal may be gold, platinum, nickel, chromium, copper or other metal or alloy and in place of the lead oxide, thallous oxide, silicon dioxide, lead borate or lead silicate may be employed as the film of insulating material. A symmetric non-ohmic conductor comprising outer layers of gold and an intermediate film of lead oxide has a voltage-amperage characteristic such as is shown in Fig. 5.

Fig. 2 shows a symmetric non-ohmic conductor in which granular material is employed. Granules 24, spherical or irregular in shape, are compressed between the externally threaded terminal or contact plates 25 that engage with the internally threaded bore or passage 26 in a sleeve or housing 27 of insulating material. Each granule is of a semi-conductor, for instance, boron carbide or silicon carbide, with a continuous coating or film of lead oxide. The film, alternatively, may be of lead silicate, thallous oxide,

lead borate or silicon dioxide. If desired, the granule may be of quartz or sillimanite coated with a metal such as gold, the gold being coated with a film of an insulating material such as lead oxide. In Fig. 3, the granules are shown compressed and bonded together in a body or member 28, as explained in greater detail hereinafter, metallic contacts 29 engaging the outer opposed surfaces of the body.

An asymmetric non-ohmic conductor in accordance with this invention is shown in cross-section by Fig. 4. It comprises a layer or plate 30 of a metal, such as platinum, having on one surface a thin film 31 of an insulating material, for example, lead oxide, a layer or plate 32 of a semi-conducting material, such as cuprous oxide, being in intimate contact with the film. The voltage-amperage characteristic of such a conductor is shown by Fig. 6. Other metals that may be employed are silver, gold, nickel, chromium and iron; other semi-conductors, silicon carbide, boron carbide, iron oxide, cupric oxide and a mixture of silicon carbide, clay and carbon.

Instead of having only one layer or plate in the device or conductor of Fig. 4 of a semi-conducting material, each of the layers separated by the film may be constituted of semi-conducting materials of different specific conductivities. For example, the conductor may comprise a film of lead oxide deposited on a plate of boron carbide, contact being made to the film surface by means of a composition of silicon carbide, clay and carbon. The voltage-amperage characteristic for such a conductor is shown by Fig. 7. A similar result can be obtained by forming thin films of lead oxide between surfaces of two other semi-conductors such as silicon carbide and iron oxide, iron oxide and cuprous oxide, or iron ferrite and a composition of silicon carbide, clay and carbon. Other insulating films, such as silicon dioxide, thallous oxide, lead borate, lead silicate, or aluminum oxide, can be used in place of the lead oxide.

It has been found that so long as the compound of which the film is composed possesses a low specific conductivity is stable, and is stoichiometrically pure, its composition is relatively unimportant. An example of this is shown in Fig. 8, where curves A, B and C are the characteristics of an aggregate of granules of silicon coated with films of lead oxide, thallous oxide, and silicon dioxide, respectively. The chemical purity of such films is important in that it has been found that the presence of small amounts of impurity in a normal insulating compound renders it a semi-conductor possessing an appreciable conductivity having a positive temperature coefficient. It would appear that it is essential that the film have a very low inherent conductivity, it having been observed that the non-ohmic properties of such an interface decrease greatly or vanish entirely when the film has a conductivity of the order of that normally associated with semi-conductors.

The production, therefore, of non-ohmic conductors from a wide variety of materials becomes possible. The problem thus becomes essentially that of producing the thin contiguous insulating films of high chemical stability at interfaces between conducting bodies. There are numerous methods available for their production. If the bodies are metallic, atmospheric or anodic oxidation will yield, in many cases, thin films of the metallic oxides. Heating granular metallic

silicon in air will produce a silicon oxide film on the granules. The characteristic of a bonded aggregate of such granules is shown by Fig. 9. Thin layers of metals can be produced on surfaces by vaporization, chemical reduction, coagulation of colloidal suspensions, electrolysis, or sputtering; and these metal surfaces can be transformed to insulating films by oxidation. Spherical quartz granules were coated with gold by sputtering and subsequently coated with lead oxide by the method described immediately hereinafter. Compressed between metallic electrodes or contact plates, an aggregate of these granules gave the characteristic shown by Fig. 10.

In some cases, metallic sulfides can be deposited in thin films on clean surfaces by coagulation of colloidal suspensions resulting from the decomposition of complex sulfur bearing salts; and these sulfides can be converted to oxides by heating in air. A film of lead sulfide can be formed on gold by immersing a gold plate or granules in a colloidal suspension of lead sulfide formed from a solution of lead acetate and thiourea by the addition of sodium hydroxide solution. The sulfide film is subsequently converted to the oxide by heating in air. The thermal decomposition of volatile organic or inorganic metallic compounds in many cases yields thin films of the metals or their oxides. For example, films of nickel can be made by heating the surface to be coated in nickel carbonyl, or iron films by heating the surface in iron carbonyl, or films of silicon by heating the surface in silicon hydride.

It is clear that non-ohmic conductors can be produced by creating on insulating bases successive layers of metals or semi-conductors and insulating materials. While films of materials such as oxides, silicates and borates have been stressed, there appears to be no reason to believe that films of other chemical compounds could not be used provided they are chemically stable and of low specific conductivity.

The above-described method of making both symmetric and asymmetric non-ohmic conductors also furnishes a means of imparting magnetic properties to such conductors, this being accomplished by using magnetic substances, such as iron, cobalt, nickel, or other alloys, or magnetic oxides or ferrites, as the bases on which the films are created. It furnishes a means for controlling the film thickness and hence the non-ohmic properties, as well as a means of studying separately the effects due to the film and those due to the base on which the film or barrier layer is deposited, this being hitherto impossible. It permits of the control of each stage, therefore, in the production of non-ohmic materials.

In the form of granular aggregates, non-ohmic conductors are not well suited to use in electrical circuits. Consequently, it is necessary to bond these aggregates in some mechanically stable matrix in such a way as to provide intimate and permanent contact between granules. The non-ohmic conductor would be in the form, therefore, of the device of Fig. 3. Among the bonds that have been employed are the thermal setting and thermal plastic organic resins, cements, glasses, silicates, borates and various ceramic compositions. The process of bonding comprises intimately mixing the bond with the non-ohmic conducting granules, pressing the mixture into a unit of the desired size and shape, and heating to a temperature to cause the bond to soften and to coalesce. To retain its original characteristics, the bonding matrix must undergo no chem-

ical or phase change, or be subject to plastic flow. In addition to these requirements, the bond must not react chemically with or tend to dissolve the compound of which the insulating film covering the granules is composed. Since the solubility of the film in a bond will depend upon temperature, the film must be insoluble in the bond at the temperature used in causing the bond to coalesce.

It has been determined that when an aggregate of film coated granules exhibiting non-ohmic conduction is bonded in a ceramic matrix in which the compound of which the film is composed is insoluble, that is, in which the film component exists as a separate phase, the non-ohmic properties of the granular aggregate are retained in the completed device. When the matrix is such that it reacts or forms a solid solution with the film component, the non-ohmic properties of the granular aggregate are either greatly diminished or disappear entirely. It is found in extreme cases that when such is the case the specific conductivity of the bonded aggregate approaches that of the granular material on which the insulating films were originally produced. These results have been obtained from studies on ceramic bonds composed of the oxides of calcium, silicon, magnesium, and aluminum, which were employed as matrices for granules of silicon carbide whose surfaces were coated with thin films of oxide of silicon. It was observed that those bonds in which silicon dioxide existed as a separate phase yielded non-ohmic materials, while those in which silicon dioxide was soluble yielded either materials less non-ohmic or practically ohmic possessing much greater conductivities.

An example of the effect of the bond on the non-ohmic conducting properties of a non-ohmic conductor is the following. Granules of silicon carbide were heated in air to produce a film of silicon dioxide on their surfaces. These granules, when subsequently compressed between metallic electrodes, had the non-ohmic characteristics shown in curve A of Fig. 11. When these granules were bonded with a mixture of the oxides of calcium, silicon, and aluminum in which silicon dioxide was insoluble, the non-ohmic characteristics shown in curve B were obtained. When similarly treated silicon carbide granules were bonded with a mixture of calcium, aluminum, and silicon oxides, in which silicon dioxide was soluble, the characteristics were those shown in curve C. In this case, the conductor has lost most of its non-ohmic characteristics and becomes more conducting due to the removal of the insulating film from the silicon carbide granules by the bond. Curve B shows essentially the same non-ohmic characteristics as curve A for the unbonded granules because the bond chosen has not disturbed the essential insulating film.

An additional example of the effect of the solubility of the surface film in the bond on the non-ohmic characteristics of bonded granules is found in the case of granules of silicon coated with lead oxide bonded in mixtures of lead oxide and silica. In those cases where the ratio of lead oxide to silica was greater than that necessary to form lead silicate the bonded aggregates were non-ohmic as shown in curve D of Fig. 12. When less than the necessary amount of lead oxide was present, the bonded aggregates were less non-ohmic and of higher conductivity as shown by curve E. Bonds such as "bakelite" and victron in which, of course, the films such as

silica and lead oxide are insoluble have been successfully employed as matrices for coated granules. The disadvantage of thermal setting or thermal plastic bonds is that they tend to soften or decompose at relatively low temperatures and hence are not generally applicable.

If the matrix in which the aggregate of film coated granules is embedded possesses an appreciable conductivity it has been found that the conductivity of the non-ohmic conductor is increased while its non-ohmic properties are decreased. By varying the conductivity of the matrix by the addition, for example, of powdered conducting substances, wide variations in the conductivities of the bonded aggregates can be realized, such variations being invariably associated with changes in the magnitude of the non-ohmic properties. Thus, ceramic materials containing powdered conducting substances may be used as bonds for non-ohmic granular aggregates provided neither the ceramic matrix nor the conducting substance added to it reacts with or tends to dissolve the film component. In like manner, semi-conductors may themselves be employed as bonding matrices subject to these conditions. As a consequence, the nature of the bonding matrix is to a large extent definitive of the resultant non-ohmic properties of non-ohmic granular aggregates embedded in this matrix.

In non-ohmic conductors composed, for instance, of granules of silicon carbide embedded in ceramic, inorganic or organic matrices, as the specific conductivity of the material at any given voltage is increased by suitable treatment during its production, the non-ohmic properties of the conductor are reduced in magnitude. That is, for any given non-ohmic material there exists an inverse relationship between the value of the conductivity and the magnitude of the non-ohmic properties. Since conductors of widely varied conductivities possessing non-ohmic properties of essentially the same magnitude are desirable, it would be advantageous to be able to vary the conductivities of the conductors over wide limits without changing the degree of departure from Ohm's law.

It has already been pointed out that rectification or asymmetric non-ohmic conduction is obtained when two conducting bodies of different specific conductivities are separated by a physically thin film of a material possessing a low specific conductivity. This is true even in the case of two semi-conductors separated by such a film. It has been found, furthermore, that when two identical substances are separated by such a film, the differential conductivity of the system is a function of the specific conductivity of the substances between which the film exists. By differential conductivity is meant the value of the conductivity as derived from the slope of the current-voltage characteristic; it will be referred to as the absolute conductivity at any specified voltage.

In the case of an asymmetric non-ohmic conductor, the conductivities for opposite polarities of the same applied potential differ because of this effect. The conductivities in opposite directions are functions of the electron concentrations and distributions in the two substances and of the ease with which electrons from either substance pass through the film to the other. Consequently, if identical films serve as the interfaces between two bodies of the same metal in one case and between two bodies of the same semi-conductor in another, the absolute conduc-

tivity of the film in the first case would be greater than that in the second. The essential point, however, is that, if in each case the film has the same thickness, the non-ohmic properties of the

two conductors are virtually identical even though their absolute conductivities are widely separated. The properties of non-ohmic materials, therefore, can be put under two general classifications: (1) The non-ohmic properties of symmetrical non-ohmic conductors are dependent on the specific conductivity of the film component and on the film thickness; (2) the absolute conductivities are dependent on the specific conductivities of the bases on which the films are deposited. It is apparent that by creating identical films on the surfaces of materials of varied specific conductivities, the absolute conductivities of the resulting non-ohmic conductors will be direct functions of the specific conductivities of these materials.

It has been found that either metals or semi-conductors can be employed equally well as bases on which thin films are deposited in making non-ohmic conductors. For example, granules of metallic silicon may be coated with thin films of silicon dioxide by being heated in air, and, thereafter, bonded in a phenol condensation product by mixing it with 20 percent by weight of moulding powder and moulding. The voltage-current characteristic for this bonded aggregate is shown by curve A of Fig. 13. As a further example, granules of silicon carbide may be coated with films of silicon dioxide by heating them in air, and similarly bonded. The voltage-current characteristic for the latter bonded aggregate is shown by curve B of Fig. 13. The absolute conductivities of the resultant conductors differ by a factor of about twenty thousand which is the same as the ratio between the specific conductivities of silicon and silicon carbide. The non-ohmic properties of the two are, however, essentially the same.

Films of lead oxide may be deposited on granules of silicon carbide, boron carbide and silicon. The absolute conductivities of the resultant non-ohmic conductors are in direct relation to the specific conductivities of the bases on which the lead oxide was deposited, the non-ohmic properties being the same for all these, as shown by the characteristic curves of Fig. 14. When bonded in a matrix of lead silicate and lead oxide, the granular aggregates evidenced the same behavior.

Other conducting bases may be used with equally good results. Among those readily available are the carbides of metals such as tungsten, titanium, and zirconium, metallic oxides such as those of iron, copper, or nickel, and other compounds, such as ferrites. Semi-conductors of widely varied specific conductivities can be produced from mixtures of oxides, ferrites and carbides; or, in general, by adding controlled amounts of impurities either in the form of separate compounds or as elements to normally non-conducting materials. The bases can be made, also, by creating films of semi-conductors on the surfaces of metallic, ceramic or other granules. By forming thin films of materials possessing low specific conductivities on the surfaces of these bases, non-ohmic conductors of widely varied conductivities possessing equivalent non-ohmic properties can be produced. In addition, by properly choosing the bases, magnetic or other properties can be imparted to the non-ohmic materials.

While this invention has been disclosed with reference to various specific embodiments thereof, it will be understood that the scope of the invention is to be considered as limited by the appended claims only.

What is claimed is:

1. An electrical conductor having non-ohmic characteristics for a potential range from a few volts to a few hundred volts, said conductor comprising conductive granules, each of which is completely coated with a thin film of a material having a low conductivity such as is normally associated with insulators, and a bond for bonding the granules together and in which the insulating film is insoluble.

2. An electrical conductor having non-ohmic characteristics for a potential range from a few volts to a few hundred volts, said conductor comprising conductive granules, each of which is completely coated with a thin film of a material having a low conductivity such as is normally associated with insulators, and a bond for bonding the granules together and which does not react chemically with the film.

3. An electrical conductor having non-ohmic characteristics for a potential range from a few volts to a few hundred volts, said conductor comprising conductive granules, each of which is completely coated with a thin film of a material having a low conductivity such as is normally associated with insulators, and a ceramic bond for bonding the granules together and which does not react chemically with the film.

4. An electrical conductor comprising an aggregate of granules of conductive material each completely coated with a thin film of silicon dioxide.

5. A non-ohmic conductor comprising granules of conductive material, a thin continuous insulating film on each granule, and a thermosetting resin bond intimately uniting said particles.

6. A non-ohmic conductor having a range of conductivity for use in electrical circuits which comprises granules of a material having the desired range of conductivity, a thin continuous insulating film on each of said granules, and a bond for intimately bonding the granules into a unit.

7. A non-ohmic electrical conductor compris-

ing an aggregate of granules of silicon each coated with a thin film of silicon dioxide and intimately bonded in a ceramic matrix.

8. A non-ohmic conductor comprising granules the surface of each of which is conductive, a thin continuous insulating film on each granule and a ceramic bond for intimately uniting the filmed granules.

9. A non-ohmic conductor having high conductivity comprising granules of a metal of high conductivity, a thin continuous insulating film on each of said granules, and a ceramic bond intimately uniting said filmed granules.

10. A non-ohmic conductor having a low conductivity comprising granules of semiconducting material, a thin continuous insulating film on each of said granules, and a ceramic bond intimately uniting said filmed granules.

11. A non-ohmic conductor comprising particles of an insulating material, a layer of a conducting material on each particle, a thin layer of an insulating material on each layer of conducting material, and means intimately bonding said particles into a unit.

12. A device for controlling the flow of electric current comprising a body of granules having crystalline silicon carbide bodies and surfaces composed of disintegrated portions of the crystalline structure and consisting primarily of silica free from a portion of the carbon normally present in silicon carbide surfaces.

13. A device for controlling the flow of current comprising a body of grains having crystalline silicon carbide bodies and having surfaces resulting from the decomposition of portions of the crystalline structure into silica and carbon and the elimination of a portion of the liberated carbon.

14. A device for controlling the flow of electric current including a current-carrying mass of crystalline, valve action silicon carbide granules having integral oxidized surfaces containing oxide, principally silica, on the granules.

15. A device according to claim 14 comprising a body of grains having crystalline silicon carbide cores and having surfaces composed of disintegrated portions of the crystalline structure converted into oxide consisting principally of silica.

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