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AMPHOTERIC COMPOUNDS

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The present invention relates generally to double-metal compounds, and particularly their application to discharge tube cathodes or filaments; and further to methods and materials for fabricating coated cathodes or filaments intended to emit electrons when heated.

A particular object of our invention is the provision of coated cathodes or filaments that will maintain for a long time high orders of electron emission at not too high temperatures; that is, cathodes or filaments that effectively resist disintegration, volatilization, and/or evaporation, particularly in the presence of ionic bombardment, and which at the same time are good electron emitters at reasonably low temperatures.

A further object is the provision of a variety of coatings for cathodes or filaments having different electron emission temperatures and disintegration and/or evaporating temperatures, as well as different characteristics of other kinds, whereby proper selection may be made depending upon the mode of operation and kind of service of the tubes with which employed.

Another object is to include among the possible double-metal compounds used for the coating compounds those with metalloids other than oxygen in such way as to be certain that these compounds are formed and maintained in lieu of the oxides.

It is well known from the investigations of Prof. Wehnelt, the German scientist, that the oxides, chlorides and fluorides of the metals of the alkaline earths have high electron emission at comparatively low temperatures, but that the active life of cathodes or filaments coated with such compounds is more or less limited for lack of resistance against disintegration, volatilization, and evaporation. Later investigations found like characteristics in other simple compounds such as the carbids and arsenides (generally alkali metal or metals of the alkaline earths plus a metalloid).

In Patent No. 1,817,636, issued August 4, 1931, in which one of us is joint inventor, it is disclosed that the compounds in which the element is one of the alkaline metals and the radical of which is an anhydride of one of the amphoteric hydroxides possess good electron emitting characteristics at but slightly higher temperatures than the sim-

ple compounds previously mentioned, and in addition have the most desirable characteristic of effectively resisting disintegration even to the extent that they withstand ionic bombardment within useful limits, and do not injuriously evaporate at the even higher temperatures required for desirable electron emission.

For these reasons it has now become possible to fabricate ionic discharge tubes, like so called "gas-filled" tubes for rectifying purposes, using cathodes or filaments coated with such compounds as barium zincate, barium nickelate, or barium aluminate, and more complicated compounds including calcium and strontium, which even under the much more severe mode of operation show in service high efficiency and satisfactorily long active life.

The appreciation of the satisfactory characteristics of these oxide compounds did not solve all of the practical desirable applications of such compounds to cathodes and filaments of useful tubes. It has previously been mentioned that these compounds require a slightly higher temperature than do the simple compounds to have the same emission. For example, a cathode operating with barium oxide will give the same emission at about 650° C. as a cathode coated with the compound barium nickelate at about 850° C. The excess heating current required for the latter is not a matter of great importance from either an economical or constructional point of view. On the other hand there is obtained a most important durability advantage in increasing the resistivity of the cathode, and in fact an extended use is had in that a cathode of this character will withstand the severe ionic bombardment necessary to the operation of a gas-filled tube.

We have found that an important factor in the matter of resistivity of the cathode against destruction is that of heat conductivity, this apparently because the energy of impact of an ion tends to generate a localized high temperature at points of impact, and in order to avoid high localized temperatures it is necessary that the heat be rapidly transmitted to other regions of the cathode structure. A material which has the characteristic of increasingly conducting heat with increase of temperature is ideally adapted to avoid the localized high temperatures, and we have found that compounds as hereinafter de-

fined possess this desirable characteristic, and to different degrees in different compounds. There is the further important factor that the materials have a sufficiently high temperature of evaporation or volatilization above the temperature required for adequate electron emission to give a factor of safety, it being well to appreciate that the operating temperature may rise higher than that originally required for electron emission for starting, this because of the heat supplied by ionic bombardment after the tube is in operation. Also the material should have the capacity of retaining that atomic arrangement that assures its emissivity at the desired temperature.

Tubes for a variety of uses require different degrees of these several factors, as well as different relations of them, so that for general application it is important that provision be had for varying these factors and their relations over a wide range as exigencies of use of tubes may require. In other words, the character of a cathode material may be expressed as a function of its emission temperature, its vaporizing temperature, and its temperature-heat conductivity characteristic.

We have found that the compounds referred to in the previously mentioned patent provide for only a limited range of change of the special character of the cathode, and have further found that by extending those compounds to those including metalloids other than oxygen, such as the nitrides, carbides, sulphides, arsenides and fluorides, or their mixtures, we can satisfy the requirements of tubes of the widest variety, and thus accommodate them with better advantage and higher efficiency to their particular uses.

There were the further problems of forming and activating such compounds on the cathode or filament structures of the various kinds in such tubes so that they would better remain chemically constant with high emission, and be of such physical characteristics as to firmly adhere to the supporting surface and better withstand the ionic bombardment of intended use, which problems were solved by the ionic bombardment forming process disclosed in copending application Serial No. 239,417 of December 12, 1927 of Carl J. R. H. von Wedel, a joint inventor of the present invention.

A result of the discovery of the aforementioned improved process for forming double-metal oxide compounds was the provision of a way to investigate these compounds other than the oxides referred to in the copending application previously mentioned, and which investigations have permitted arriving at some laws applicable in general to double-metal compounds.

The British scientist Richardson has characterized the electrical potential expressed in volts necessary to free electrons from an element as the "work function", and found that this potential or work function varies widely for different elements. As a result of elaborate investigations he tabulated the work functions of certain of the elements into what is now known as "Richardson's Constants", set forth in his book *The Emission of Electricity from Hot Bodies*, published by Longmans, Green and Co., 39 Paternoster Row, London, 1921. It is physically obvious that the lower the work function the more electrons a material will emit at a given temperature.

One of us has derived an empirical formula for computing these work functions, computations from which give work function values em-

pirically approximating those of Richardson. The formula is as follows:

$$\delta_e = \frac{7N^{\frac{1}{2}}}{4Z^{\frac{1}{2}}} + 1$$

in which

δ_e = the work function in volts.

N = number of valence electrons of the element.

Z = number of positive charges of the nucleus.

The N and Z values for this formula can be found in usual text books on physics covering such subject matter.

We have found that in general a compound having the desired previously outlined characteristics is one which has a chemical type of formula $X_a Y_b Z_c$ wherein X_a is a highly electropositive metal (one forming bases), for example those alkaline metals found in Groups I and II, Series 4, 6 and 8 of Mendeleef's Periodic System as compiled by Alexander Silverman and published by D. VanNostrand Company, New York, Copyright 1922; Y_b is a more or less indifferent or inactive metal (one forming salts); and Z_c is an effective metalloid binder for the two metals (a metalloid which is acid forming).

These three constituents may be further classified as X_a , those elements having a work function between 1 and 3.3 volts as tabulated in Richardson's work or computed from the formula hereinbefore set forth, of which cesium, barium, calcium, thorium, and strontium are examples; as Y_b , those metals, having relatively high work functions, of which beryllium, nickel, cobalt, chromium, and tungsten are examples; as Z_c , those elements having a work function greater than 6 volts as recorded by Richardson and computed according to the formula hereinbefore set forth, which elements may have a negative valence and are used in various chemical compounds to replace oxygen of which carbon, sulphur, arsenic, nitrogen and fluorine are examples.

This general law thus shows that many compounds not oxides, but having the desired characteristics previously pointed out, are available. We mention in particular such compounds as cesium-beryllium-sulphur, strontium-zirconium-carbon, and thorium-tungsten-arsenic.

In view of the necessity of frequently having to refer to a good or sufficient electron emission in describing this invention, we define such reference as an emission of the compound in question below a temperature of destructive character for the particular compound at least comparable to the emission of barium oxide at 650° C.

In making up the cathode or filament it does not suffice to consider the coating alone. The structure as a whole must be coordinated with the final end in view. In the patent relating to the oxides previously referred to it was pointed out that core materials may be chosen of suitable metals or alloys to form with certain compounds the desired oxides of amphoteric compounds, or that cores could have a superficial coating (electroplated or the like) of such metals or alloys. It has further been found that a core metal should not be used with a compound that will form therewith a corrosively penetrating compound. For example, a platinum core coated with barium oxide or barium nickelate will form, when heated, barium platinate which will result in a corrosive or crystalline decomposition of the body of the core. A tungsten core coated with a

compound including thorium-tungsten-arsenide will not result in core corrosion. When the compounds are placed directly on the core in some cases the inclusion in the compound of the same metal of the core will avoid this corrosion.

There are a number of metals, such as nickel, cobalt and copper, which do not form with a large number of desirable compounds corrosive compounds, and which have vaporizing temperatures in vacuum sufficiently high not to vaporize at effective emission operating temperatures of the compounds. These metals are usually too soft for the strength needed in cores. The advantages of these metals can be utilized by electroplating or otherwise coating them on the surface of the stronger metals, such as tungsten, platinum and the like, care being taken that the final metallic coating is not porous, otherwise corrosively acting compounds may penetrate to the core metal.

These soft metals in many cases form with the coating desirable compounds. For example, a plating of nickel on a metal core may form with barium carbonate and/or barium aluminate a barium nickelate, and this formation may be a gradual chemical change during the use of the tube in service. Such a transposition will not free any undesired gas, and will not seriously alter the emissivity of the barium.

In some cases it may be desirable to apply the compounds in layers on the core, more particularly in the case of oxides, in which case it is preferable to place the compound having the most highly emissive metal at the outside. The inner layer may be chosen to include a metal that has the property of binding the coating or sintering it into a hard, firmly adhering mass upon heating. For example, there may be used barium oxide, calcium oxide, and strontium oxide, each finely powdered, or each finely powdered and mixed with finely powdered nickel, the powders including a temporary binding material such as gum arabic, and in such form applied one by one to the core in the reverse order named so that the strontium, which has the hardening property, is next to the core, and the barium, which is the most emissive, is outside. The oxides of amphoteric compounds may be then finally formed on the so treated core by first heating the core in any suitable way while pumping the tube, and finally subjecting the core to ionic bombardment in a suitable gas atmosphere of suitable pressure, all described more in detail in the copending application Serial No. 239,417 previously referred to.

A specific example of our invention, but in no way limiting the scope of the invention or the claims appended to this application, is a compound in which X_a is an element having a work function of between 1 and 3.3 volts in Richardson's constants of which barium is an example; in which Y_b is one of the aforementioned metals having a high work function, for instance nickel; and in which Z_c is nitrogen. Recapitulating then, one of the compounds within our invention is barium-nickel-nitride a process of formation of which is described in detail hereinafter.

In order to bring out the manner in which an amphoteric nitride is formed, with certainty that a nitride and not an oxide actually results, an example of forming barium-nickel-nitride is given. There is preferably chosen a nickel core or other metal core plated with nickel. This wire is coated with thin layers as before described or barium-nickel-cyanide and calcium-ferrocya-

nide, or strontium-nickel-cyanide and calcium-ferrocyanide. The coated filament is heated while pumping the tube and then finally bombarded in a nitrogen atmosphere. This process assures that the final compounds are nitrides as the operation is confined to an atmosphere of nitrogen. In previous attempts to produce such nitrides no way of preventing the presence of oxygen was had with the result that the final compounds were at least partially oxides. Any later attempt to determine the character of the compound results in exposure of the cathode to oxygen by opening the tube, so that the examination discloses the presence of oxides. It is therefore only possible to assert that the emissive compound is a nitride when formed in such a way as to preclude the forming of oxides, such as we have provided.

On account of the poisonous character of the cyanides it may not be desirable under some circumstances to fabricate cathodes or filaments from such compounds. The desired nitride compounds may be formed from oxides or carbonates, as barium, calcium, strontium, together with finely powdered nickel. It is desirable to add to the mixture a more electropositive metal, such as rubidium, in order to free the oxides of oxygen, or to bind the freed oxygen. The bombardment in the presence of nitrogen is made as before, and the nitrides thus formed. The present oxygen is so bound by the electropositive rubidium that it cannot interfere with forming of the desired nitrides. In some cases it may be convenient to substitute for barium oxide substances which lose their metalloids only by heating, of which the carbonyls are examples.

In the cases of some of the compounds that may be chosen to furnish the elements for the double-metal compounds herein contemplated there is possible a combustion or thermit effect in the contemplated compounding, the heat of which may be advantageously contributed towards the necessary heat for the formation and activating processes.

Our invention may be employed to form the coatings of cathodes of any type, and including both the so-called indirect heated cathode, in which the heat from an independent filament or wire is employed indirectly to heat the cathode element proper, and the filament cathode in which the current passes through the cathode element.

For the sake of brevity and definiteness, the term "alkaline metal" used herein and in the appended claims is to be construed as generic to the "alkali metals" and "alkaline earth metals".

While we have described our invention in connection with double-metal compounds of particular value for cathode coatings, yet such compounds have other uses obvious to those skilled in the art, and we do not intend any limitations by reason of such choice for description, but only as imposed by the scope of the appended claims.

We claim:

1. An electric discharge tube having an incandescent electron emissive cathode, said cathode at least in part consisting of a compound the primary element of which is one of the alkaline metals, and the radical of which comprises a metal having a relatively high work function and nitrogen.

2. A gaseous discharge tube having an incandescent electron emissive cathode, said cathode at least in part consisting of a compound the primary element of which is one of the elements

of Group II, Series 4, 6 and 8 of the Periodic Table, and the radical of which comprises another metal and fluorine.

3. A gaseous discharge tube having an incandesable electron emissive cathode, said cathode consisting of a metallic core coated with a compound the primary element of which is one of the alkaline metals, and the radical of which consists of a fluoride of a metal which is the same element as that constituting the core.

4. An electric discharge tube having an incandescent electron emissive cathode, said cathode at least in part consisting of a compound the primary element of which is barium, and the radical of which consists of a nitride of nickel.

5. An electric discharge tube having an incandesable electron emissive cathode, said cathode at least in part consisting of a compound the primary element of which is one of the elements of Groups I and II, Series 4, 6 and 8 of the Periodic Table, and the radical of which includes a metal with a high work function and arsenic.

6. A gaseous discharge tube having an incandesable electron emissive cathode, said cathode at least in part consisting of a compound the primary element of which is one of the elements of Group II, Series 4, 6 and 8 of the Periodic Table, and the radical of which includes a metal having a high work function and fluorine.

7. A gaseous discharge tube having an incandesable electron emissive cathode, said cathode at least in part consisting of a compound the primary element of which is one of the elements of Group II, Series 6 and 8 of the Periodic Table,

and the radical of which includes a metal having a high work function and fluorine.

8. A gaseous discharge tube having an incandesable electron emissive cathode, said cathode at least in part consisting of a compound the primary element of which is one of the elements of Group II, Series 4 and 8 of the Periodic Table, and the radical of which includes an amphoteric metal having a high work function and fluorine.

9. A gaseous discharge tube having an incandesable electron emissive cathode subject to ionic bombardment, said cathode comprising at least on its surface a double-metal compound having a type formula $X_a Y_b Z_c$ in which the element X_a is an alkaline metal, the element Y_b is a metal less electro-positive and having a substantially higher work function than X_a , and the element Z_c is one of the group of non-metals which consists of carbon, sulphur, arsenic, nitrogen and fluorine; the said double-metal compound being non-vaporizable at temperatures at which said cathode has an emissivity substantially equal to the emissivity of barium oxide at 650° centigrade.

10. A gaseous discharge tube having an electron emissive cathode, said cathode comprising a metallic core coated with a double-metal compound the primary element of which is one of the alkaline metals and the radical of which consists of the core metal and one of the group of non-metals consisting of carbon, sulphur, arsenic, nitrogen and fluorine.

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