May 26, 1953 H. JACOBS ET AL 2,639,963

SECONDARY EMITTER AND METHOD OF MANUFACTURE

Filed April 5, 1948

FIG. 1

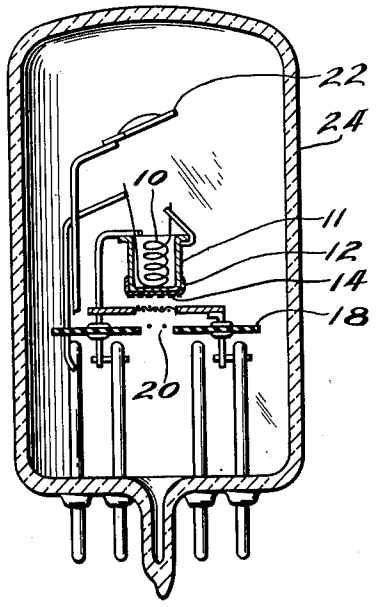
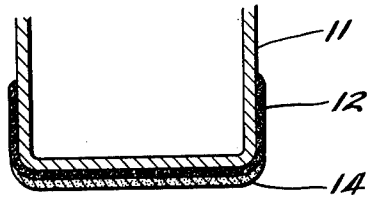


FIG. 2



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Patented May 26, 1953

2,639,963

UNITED STATES PATENT OFFICE

2,639,963

SECONDARY EMITTER AND METHOD OF MANUFACTURE

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Application April 5, 1948, Serial No. 19,004

19 Claims. (Cl. 316—19)

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This invention relates to electron emitter materials and to the method of their application to surfaces used in electron discharge devices.

Although it has been common knowledge in the electronic industry that alkaline metals are useful in promoting secondary electron emission, it has heretofore been deemed necessary to have these materials on the emitting surface in a very thin layer usually in atomic dimensions and due to inherent properties of these materials, it was considered necessary to apply these materials to the surfaces in such a way that metallic evaporation of activating agents was considered necessary, together with the subsequent bakeout of excess metal. This was done during the processing and no prefabrication of parts was considered practical inasmuch as the active metals readily combine with air.

For example, in making one of the more popular secondary emitters such as the silver oxide cesium surface, the general processing called for the use of silver electrodes. The silver in the finished tube on exhaust was then oxidized by admitting low pressure oxygen in to the tube on exhaust and a glow initiated to oxidize the silver. Uniform oxidation is a very difficult task in this part of the processing. Then a layer of cesium metal was deposited on the silver oxide surface by evaporation. Tubes were then baked in order to drive off excess cesium. After this step the surfaces were supposed to be active, ready for use as both the secondary emitter and a photoelectric emitter.

In actual practice, this method has inherent difficulties even though the secondary emission ratios may be as high as 3 to 5 at 150 volts. The first troublesome feature of the process is the introduction of oxygen and the glowing of the silver electrodes. This does not lend itself readily to mass production. The second and by far the most difficult problem to overcome when using this process is the electrical leakage frequently encountered due to free cesium vapor in the tube. Cesium metal is volatile and easily polarized, easily ionized and readily adsorbed.

In some cases experimental cesium vapor tubes have exhibited a short circuit between electrodes even though the glass or supporting structure between electrodes is visibly free of metal. When a flame was applied to the glass between the electrodes, the leakage readily disappeared due to the heating. However, the conductivity of the glass surface rose again upon cooling and the short circuit between the electrodes re-appeared, with no visual evidence of a metallic conducting path.

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Although one of the common methods of reducing electrical leakage is the so-called sparking method, in the case of cesium the sparking may easily increase the leakage indicating that cesium may be submitted to a more random distribution as though the heat of the spark caused the cesium to behave like a gas. Even such methods as placing insulating powder such as magnesium oxide or aluminum oxide on the structure between the electrodes does not seem to help. This is probably due to the high adsorption properties of cesium metal.

It is, therefore, well known in manufacturing circles that when alkaline metals such as cesium are used in tubes, several cycles of sparking, rebaking and re-flashing have to be performed to get the right balance between electrical leakage and electron emission. The electrical leakage is almost always high and often so high as to interfere with photoelectric measurements. This results in one of the primary causes of noise and dark current. The object of this invention is to provide an improved electron emissive material.

Another object of this invention is to provide a method of applying such materials to surfaces in a manner which will readily lend itself to mass production techniques.

It has been found that these objectives and other advantages can be obtained by operating in accordance with the teachings of this invention.

Figure 1 of the drawings is an elevation partly in section of an electron discharge device employing features of this invention.

Figure 2 of the drawings is an enlarged sectional view of the dynode cover and its coatings as shown in Figure 1.

In accordance therewith it is found that bulk compounds of secondary emission materials such as the alkaline metals and alkaline earth metals can be used on the surfaces to obtain copious secondary emission yet eliminating much of the vacuum processing which has previously been considered necessary as for example the flashing of cesium pellets and subsequent sparking and baking.

Although the technique and teachings of this invention can be applied to the use of the alkaline earth metals the problems of the prior art were greatest with respect to the alkaline metals. It is therefore particularly gratifying that compounds of cesium which in addition to having the highest electron emissivity of the alkaline metals, is the most active of all metals and also the most electropositive, can readily be applied by

the method of this invention. This is further gratifying in that cesium has a reputation for being one of the most difficult metals to handle particularly on a commercial scale where it is economically unsound practice to have to resort to sparking and baking techniques and where leakage problems cannot be tolerated. Since cesium has been recognized as being one of the most difficult of the metals to handle, it will readily be apparent that whenever cesium is given as an example in this specification any of the other alkaline metals as well as the alkaline earth metals could be substituted therefor.

The most satisfactory compounds are those which can be activated by the heat treatment, for example, the carbonates, fluorides and chlorides (i. e. CsF, BaF_2, Cs_2CO_3, $BaCl_2$, $BaCO_3$). The carbonates readily lend themselves to decomposition by heat treatment to form the oxides. The oxides in turn by further heating become activated. It was found that the above-noted compounds can be coated in bulk form on electrode materials which upon heat treatment give good secondary emitters upon electron bombardment photoelectric emitters and thermionic emitters and gas tube cathode emitters. When so used, the compounds may be coated on the metal forming the electrode in bulk either by cataphoresis or spraying.

After the electrode has been coated by one of these methods, and is heated on exhaust to approximately 800 degrees C. ± 200 degrees brightness for two minutes copious thermionic emission can be obtained. This can further be enhanced by bombardment with electrons. On numerous occasions some thermionic emission was noticed at as low as 200 degrees C. at about 100 microamperes per square centimeter where cesium carbonate had been coated on nickel.

The metal upon which the carbonate is deposited may play an important role in effecting the emissive properties of the coating material, for example in some instances it has been found that barrier layers of relatively inert metals having low heats of formation in oxide form such as rhodium, platinum, silver, gold and copper when placed on the metal support between the electrode and the coating tend to enhance the secondary emission. It also reduces the thermionic emission. The cathode nickels containing reducing agents, increase the thermionic emission but reduce the secondary emission.

In the course of several experiments which were carried out in which cesium carbonate was deposited by spray methods on rhodium plated nickel surface, it was found that secondary emission ratios of the order of three at 150 volts at room temperature with approximately 50 microamperes striking the surface for a period of at least 400 hours, can be obtained. During this four hundred hour period, the secondary emission ratio remains practically constant.

Although the oxides formed on the electrodes as a result of decomposition of the compounds of the alkaline and alkaline earth metals, and the carbonates thereof, have proven to be excellent emitting materials, it is further gratifying that these emissive properties can further be enhanced by adding impurities to the metal compounds of the coating before they are activated by heating. For example, upon the addition of potassium carbonate to cesium carbonate it is found that the secondary emission ratio can be enhanced from a value of three at 150 volts to a value of four at 150 volts. The percentage concentration in mol percent for this particular material may be on the order of 50% for each. The percentage is not critical.

Silver compounds have also been found to be a desirable addition. For example tubes prepared by mixing silver oxide powder with cesium carbonate and then spraying the substance on the dynode prior to mounting on the tube gives excellent results after processing. Processing may for example consist of mounting the dynode, sealing it into place, placing it on exhaust, and heating for approximately two minutes at a full red heat.

The tube may then be heated in such manner that the getter is flashed and following this the tube may be tipped off. It was found that although the secondary emission may be relatively low initially that is, 1.5 to 3 at 150 volts with 15 microamperes striking the dynode at room temperature after operating at approximately one half hour at 150 volts, 50 microamperes to the dynode at room temperature the secondary emission will rise to a very high value. For example it is not uncommon after a day of operation that the ratio should rise to 9 to 1 at 200 volts; 7.5 to 1 at 150 volts and 5 to 1 at 100 volts. In fact results have been obtained wherein tubes which have been aged approximately seven hours have shown a ratio of 18 to 1 at 200 volts, 16 to 1 at 150 volts and 10 to 1 at 100 volts.

Although it is possible to work with cesium compounds in accordance with the method of this invention and avoid the problems previously encountered, the deliquescent nature of alkali metals and their compounds raises certain other problems particularly in the summer months when the weather is warm and the humidity is high. During this period the material will pick up water, tend to run, conglomerate and change physical appearance.

In general the application of any spraying mixture or more precisely suspension is preceded by a period of ball milling, whereby the overall particle size of the solid is reduced. It was found, however, as a result of repeated tests that although the carbonate of cesium is initially a white crystalline material its physical appearance following however brief a milling period was measurably altered. Further investigation led to the fact that the transformation from a white crystal to a yellow-orange-brown amorphous mass occurs in the presence of nitrocellulose.

This reaction does not seem to take place in the presence of any one of the other organic solvents commonly used to spray suspensions. This observation combined with the fact that the cesium compounds are highly polar molecules may explain the reason for the apparent anomaly. Transformation and reaction of these polar cesium molecules therefore makes their application on metal surfaces impractical in the presence of nitrocellulose. The total reaction in time in such a transformation, incidently, depends on the nitrocellulose concentration in the lacquer but the initial stages will appear within one or two minutes after the mixing.

On the basis of these observations, it would seem that one feasible method for applying cesium compound to metallic surfaces is to first reduce their particle size by conventional ball milling methods in a medium solvent such as amyl acetate and then to apply the material by spraying the lacquer free suspension. The coated metal surface could then be rendered im-

pervious to atmospheric moisture and absorption by applying a thin coat of protective lacquer.

However, this method is not entirely satisfactory. It still forms lumps, tends to run over the mica supporting structure on which it may be mounted in an electron tube and is difficult to degas.

Another method has been worked out, in accordance with which ethylcellulose and amyl acetate are used as the suspending medium. It has been found that if this is done, alkali metal compounds including those of cesium, after being milled can be permitted to stand for weeks and after rolling an hour still retain the nature and consistency suitable for spraying and electrophoretic deposition.

An example of a spray suspension which has consistently been used with success is made up as follows: Cesium carbonate—four parts by weight; silver oxide—one part by weight; amyl acetate—five parts by volume; ethylcellulose—4.6 parts by weight in amyl acetate—5 parts by volume. Milling time is 24 hours.

In accordance with another preferred embodiment of the spray solution of this invention, 50 cc.'s of 4.6 percent ethylcellulose in amyl acetate is added to 50 grams of 80% cesium carbonate and 20% silver oxide whereupon a further addition of 50 cc.'s of amyl acetate can be added. The total formula is then milled for a period of 48 hours. This mixture, upon being sprayed on nickel surfaces, appears to be stable in air during the sealing processes.

The drawing shows an experimental tube of the type in which the secondary emission measurements were made in the laboratory.

This tube contains a filament 10 mounted within a dynode cup 11 onto the bottom of which the barrier coating 12 and emissive coating 14 have been formed. A tungsten 100 mesh grid 30 covers a ⅛ inch diameter hole positioned between the dynode cup 11 and the tungsten filament 20 mounted in the mica support 18. A getter 22 positioned near the top of the tube envelope 24 was used in the usual manner to clean up the residual gases after the degassing operation.

In the preparation of a specific tube embodying features of this invention, the dynode cup prior to mounting was coated with a thin film of rhodium 12 and subsequently sprayed with a relatively thick coat of cesium carbonate 14 whereupon the components of the tube were mounted in the envelope and the tube baked out at a temperature of 400 degrees for about ½ hour. Subsequently the envelope was degassed and kept at a temperature of 800 degrees C. brightness for one minute. The dynode was then heated by means of the filament 10 for a period of approximately 2 minutes at a temperature of about 800 degrees C. whereupon the getter was flashed and the tube tipped off. The tube was then aged by bombarding the grid with electrons for three minutes with sufficient current on to degas the grid.

While the above description and drawings submitted herewith disclose preferred and practical embodiments of the secondary emission dynodes and their method of manufacture, it will be understood by those skilled in the art, that the specific details of manufacture as shown and described are by way of illustration and are not to be construed as limiting the scope of the invention.

What is claimed is:

1. A secondary electron emissive electrode suitable for use in electron discharge devices upon being mounted therein and subjected to heat treatment comprising a base metal, a barrier layer of relatively inert metal selected from the group consisting of rhodium, platinum, silver, gold and copper and a bulk coating of an alkali metal carbonate.

2. A secondary electron emissive electrode suitable for use in electron discharge devices upon being mounted therein and subjected to heat treatment comprising a base metal, a barrier layer of a relatively inert metal selected from the group consisting of rhodium, platinum, silver, gold and copper and a bulk coating of an alkaline earth metal carbonate.

3. A secondary electron emissive electrode suitable for use in electron discharge devices upon being mounted therein and subjected to heat treatment comprising a base metal, a barrier layer of a relatively inert metal selected from the group consisting of rhodium, platinum, silver, gold and copper and a bulk coating of cesium carbonate.

4. A secondary electron emissive electrode suitable for use in electron discharge devices upon being mounted therein and subjected to heat treatment comprising a base metal, a barrier layer of a relatively inert metal selected from the group consisting of rhodium, platinum, silver, gold and copper and a bulk coating of cesium fluoride.

5. The method of making a secondary emissive electrode which comprises coating a base metal with a mixture of alkali metal carbonates and mounting the electrode within a tube exhausting the tube and subjecting the coated electrode to a heat treatment to break down the carbonate to form the oxides of the alkali metals, having a surface capable of giving copious secondary electron emission.

6. The method of making a secondary emissive electrode which comprises coating a base metal with a mixture of an alkali metal carbonate and silver oxide mounting the electrode within a tube exhausting the tube and subjecting the coated electrode to a heat treatment to break down the carbonate to form the oxide of the alkali metal to produce a surface capable of giving copious secondary electron emission.

7. The method of making a secondary emissive electrode which comprises coating a base metal with a mixture of cesium carbonate and potassium carbonate, mounting the electrode within a tube, exhausting the tube and subjecting the coated electrode to a heat treatment to break down the carbonates to form the oxides to produce a surface capable of giving copious secondary electron emission.

8. The method of making a secondary emissive electrode which comprises coating a base metal with a mixture of cesium carbonate and silver oxide, mounting the electrode within a tube exhausting the tube and subjecting the coated electrode to a heat treatment to break down the carbonate to form the oxide to produce a surface capable of giving copious secondary electron emission.

9. The method of making a secondary emissive electrode which comprises coating a base metal with a mixture of an alkaline earth metal carbonate and silver oxide, mounting the electrode within a tube exhausting the tube and subjecting the coated electrode to a heat treatment to break down the carbonate to form the oxide of the alkaline earth metal to produce a surface

capable of giving copious secondary electron emission.

10. The method of making a secondary emissive electrode which comprises coating a base metal with a relatively inert metal selected from the group consisting of rhodium, platinum, silver, gold and copper, superimposing a mixture of an alkali metal carbonate, mounting the electrode within a tube exhausting the tube and subjecting the coated electrode to a heat treatment to break down the carbonate to form the oxide to produce a surface capable of giving copious secondary electron emission.

11. The method of making a secondary emissive electrode which comprises coating a base metal with a relatively inert metal selected from the group consisting of rhodium, platinum, silver, gold and copper, superimposing a mixture of a cesium carbonate and silver oxide, mounting the electrode within a tube exhausting the tube and subjecting the coated electrode to a heat treatment to break down the carbonate to form the oxide to produce a surface capable of giving copious secondary electron emission.

12. The method of making a secondary emissive electrode comprising suspending an alkali metal carbonate in a solution of ethylcellulose in amyl acetate applying the suspension to a base material, mounting the coated material in a tube and subsequently heating the coating to break down the carbonate to the oxide to produce a surface capable of giving copious secondary electron emission.

13. The method of making a secondary emissive electrode comprising suspending cesium carbonate in a solution of ethylcellulose in amyl acetate applying the suspension to a base material, mounting the coated electrode in a tube and subsequently heating the electrode to break down the carbonate to the oxide to produce a surface capable of giving copious secondary electron emission.

14. The method of making a secondary emissive electrode comprising suspending a mixture of cesium carbonate and silver oxide in a solution of ethylcellulose in amyl acetate applying the suspension to a base material, mounting the coated material in a tube and subsequently heating the coating to break down the carbonate to the oxide to produce a surface capable of giving copious secondary electron emission.

15. The method of making a secondary emissive electrode comprising suspending a mixture of alkali metal carbonates in a solution of ethylcellulose in amyl acetate applying the suspension to a base material, mounting the coated material in a tube and subsequently heating the coating to break down the carbonates to the oxides to produce a surface capable of giving copious secondary electron emission.

16. The method of making a secondary emissive electrode comprising coating a base metal with a barrier layer of a relatively inert metal selected from the group consisting of rhodium, platinum, silver, gold and copper, suspending an alkali metal carbonate in a solution of ethylcellulose in amyl acetate applying the suspension to said barrier layer, mounting the coated metal in a tube and subsequently heating the coating to break down the carbonate to the oxide and thereby obtain a surface capable of giving copious secondary electron emission.

17. The method of making a secondary emissive electrode comprising coating a base metal with a barrier layer of a relatively inert metal selected from the group consisting of rhodium, platinum, silver, gold and copper, suspending a mixture of alkali metal carbonates in a solution of ethylcellulose in amyl acetate applying the suspension to said barrier layer, mounting the coated metal in a tube and subsequently heating the coating to break down the carbonates to the oxides to produce a surface capable of giving copious secondary electron emission.

18. The method of making a secondary emissive electrode comprising coating a base metal with a barrier layer of a relatively inert metal selected from the group consisting of rhodium, platinum, silver, gold and copper, suspending a mixture of cesium carbonate in a solution of ethylcellulose in amyl acetate applying the suspension to said barrier layer, mounting the coated metal in a tube and subsequently heating the coating to break down the carbonate to the oxide and thereby obtain a surface capable of giving copious secondary electron emission.

19. The method of making a secondary emissive electrode comprising coating a base metal with a barrier layer of a relatively inert metal, selected from the group consisting of rhodium, platinum, silver, gold and copper, suspending a mixture of cesium carbonate and silver oxide in a solution of ethylcellulose in amyl acetate applying the suspension to said barrier layer, mounting the coated metal in a tube and subsequently heating the coating to break down the carbonates to the oxides to produce a surface capable of giving copious secondary electron emission.

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