

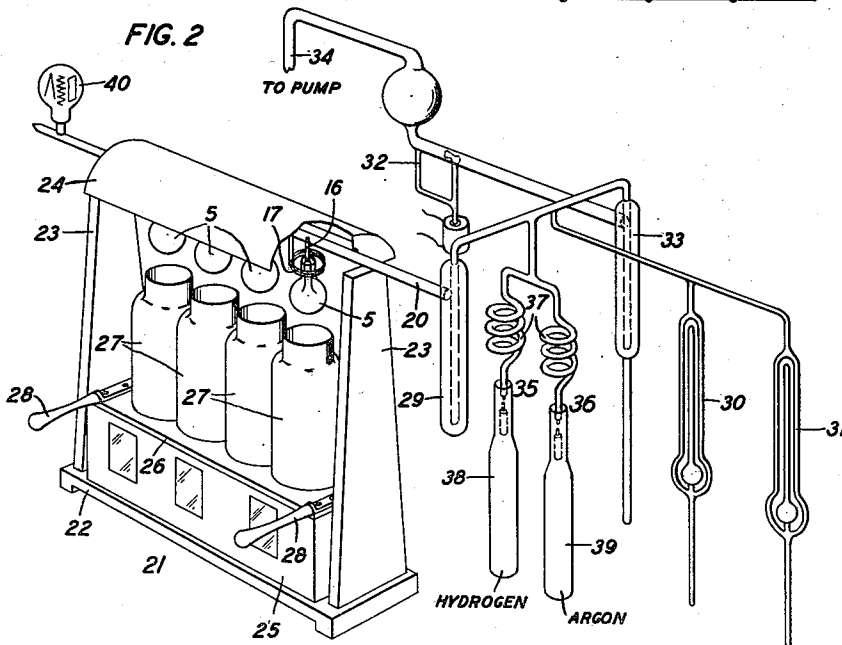
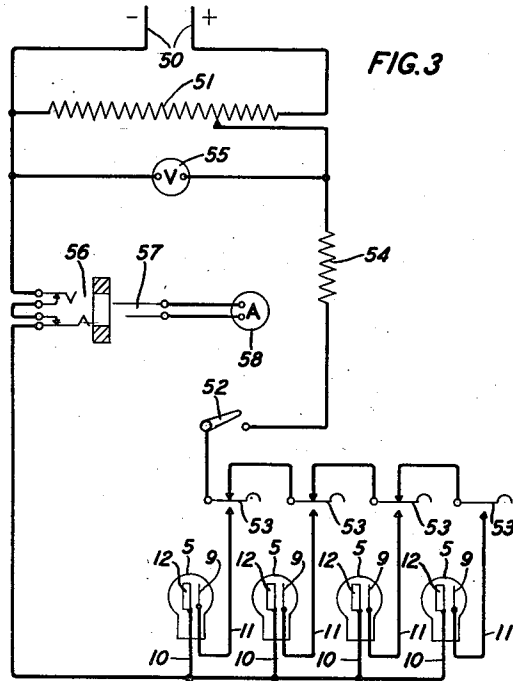
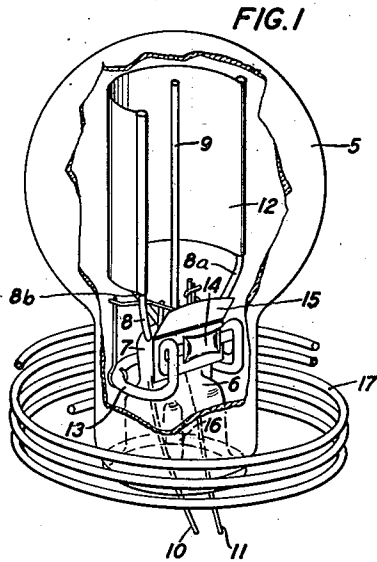
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PHOTOELECTRIC TUBE

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PHOTOELECTRIC TUBE

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This invention relates to photoelectric tubes and more particularly to cathodes of the composite type for such tubes and methods of making such cathodes.

5 An object of the invention is to provide an improved cathode of the composite type.

A method of preparing a cathode, according to this invention, comprises providing on a metallic support a coating of a mixture of an easily reducible metallic compound and a refractory compound, reducing the easily reducible compound by heat to leave minute particles of the metal intimately mixed with the refractory compound, and then impregnating the resulting layer with an alkali metal by heating the layer and metallic support in the presence of alkali metal vapor. Suitable easily reducible metallic compounds are silver oxide, tin oxide and copper oxide. Suitable refractory compounds are zirconium oxide, aluminum oxide and aluminum silicate. These refractory compounds are stable with respect to the atmosphere and fall within that class of compounds which may be called "insoluble metal oxygen refractories." These compounds are particularly useful in applicant's invention, not only because they are unchanged by high temperatures, but also because they are not affected by moisture which is always present in the atmosphere. The reduction of tin and copper oxides is advantageously effected in an atmosphere of hydrogen. Tin and copper are examples of "base metals," the oxides of which are reducible by heat only in a reducing atmosphere such as an atmosphere of hydrogen.

35 This invention makes possible a more accurate control of the ingredients comprised in a composite matrix for an electron emitting cathode. Furthermore, a much more stable cathode comprising an alkali metal as a constituent is provided.

40 A more detailed description of the invention follows having reference to the accompanying drawing.

Fig. 1 illustrates a photoelectric tube embodying this invention;

45 Fig. 2 shows a pump station suitable for processing four tubes concurrently; and

Fig. 3 is a schematic electric circuit for measuring the sensitivity of any one of four tubes during the processing operation.

50 The photoelectric tube illustrated in Fig. 1 comprises a glass bulb 5 having a reentrant stem 6 sealed therein. The stem 6 is provided with a press 7 in which are sealed cathode support wires 8, 8a and 8b, and anode wire 9. Lead-in

wires 10 and 11 are connected to support wire 8 and anode wire 9 respectively. Cathode 12 comprises a semi-cylindrical plate, the straight edges of which are rolled around the support wires 8 and 8a, and to the lower rear edge of which support wire 8b is connected. Also supported by wires sealed into the press 7 is a heavy copper wire 13 which partially encircles the stem 6 and between the ends of which is a metallic capsule 14. This capsule 14 encloses a mixture for producing caesium vapor when heated. A nickel shield 15 is supported also from wires sealed into the press 7 between the capsule 14 and the press 7 and concave surface of cathode 12. This stem 6 is provided with an exhaust tube 16.

15 The coil 17 is used to induce current in the copper wire 13 and capsule 14 for heating the mixture within the capsule to its reaction temperature. This coil 17 is used only during the processing of the cathode 12 and is shown partially broken away in Fig. 1. A portion of the glass bulb 5 is shown removed also for clearness of illustration.

20 The electrode and accessory structure carried by the stem 6 is fabricated before the stem is sealed into the glass bulb 5. The anode 9 is a nickel wire substantially coaxial with the concave cylindrical surface of the cathode 12.

25 The caesium producing mixture within the capsule 14 is in the form of a compressed pellet. It is composed of approximately 15 milligrams of caesium chromate, Cs_2CrO_4 , 20 milligrams of chromic oxide, Cr_2O_3 , and 11 milligrams of powdered aluminum, Al. These ingredients are carefully prepared, finely pulverized and thoroughly mixed in the proper proportions before being compressed into pellets.

30 The pump station illustrated in Fig. 2 is adapted to the processing of four tubes concurrently. The bulbs 5 are sealed to a glass header 20 by exhaust tubes 16. This header 20 runs through an oven 21 which comprises a base 22 carrying end supports 23, on the upper ends of which is a metallic cap 24. An electric heater 25 between the supports 23, 23 is surmounted by removable cover 26, carrying four chimneys 27. This cover is provided with handles 28. The heater 25, cover 26 and chimneys 27 may be raised as a unit so that the chimneys surround the bulbs 5. Each chimney is provided with a slidable baffle (not shown) to control the convection air currents flowing through the associated chimney. With the cover 26 and chimneys 27 removed, the heater 25 may be raised up against the cap 24 to completely surround the bulbs 5. The header

20 is connected to pumping apparatus comprising a liquid air trap 29, two McLeod gauges 30 and 31, a mercury vapor pump 32, a mercury cut-off 33, and a vacuum pump (not shown) connected to tube 34. Between the mercury cut-off 33 and the liquid air trap 29, two gas supply units 35 and 36 are connected to the pumping apparatus. Each unit comprises a flexible coiled glass tube 37. Unit 35 comprises a container 38 for hydrogen. Unit 36 comprises a container 39 for argon. Each flexible tube 37 is associated with a container 38 or 39 through a mercury seal surrounding a pair of porous plugs of "Lavite" which when brought together permit gas to pass from the container to the associated glass coil 37. An ionization manometer 40 is connected to the other end of the header 20.

An electrical circuit used during the processing of four tubes while they are sealed on the pump station is illustrated in Fig. 3. This circuit comprises conductors 50 adapted to be connected to a direct current source (not shown) and a potentiometer 51 for determining the potentials to be impressed across electrodes 9 and 12 of tubes 5. With the switch 52 closed positive potential may be impressed on any one of the anodes 9 of tubes 5, by closing the lower contact of a switch 53, which is individual to the associated tube. The voltage determined by potentiometer 51 is indicated by voltmeter 55. The current flowing through the tubes 5 may be determined from ammeter 58 when plug 57 is inserted in jack 56.

In accordance with this invention a variety of specific methods may be employed, all of which produce a composite matrix of alkali metal associated with a mixture of finely divided metal and inert refractory material. Three specific methods will now be described. It will then be obvious how the general method can be used in other specific ways.

The specific method first to be described produces a cathode containing caesium, silver and zirconia. The nickel cathode 12 has its concave surface roughened by sandblasting or by oxidation and reduction. This roughened nickel surface is coated with a suspension of silver and zirconium oxides in water to which a small amount of zirconium nitrate has been added. The ingredients, silver oxide, zirconium oxide and zirconium nitrate, are thoroughly ground together in a ball mill. After grinding the suspension is applied to the concave surface of the cathode 12 by a compressed air spray gun and gently dried. In drying, the zirconium nitrate serves to bond the coating together.

The concave surface of the cathode 12 has an area of approximately $2\frac{1}{2}$ square inches. About 15 per cent of silver oxide and 85 per cent of zirconium oxide are used in the suspension.

The stem assembly including the coated cathode 12 is then sealed into the bulb 5 and four assembled tubes at a time are sealed onto the pump station, as shown in Fig. 2. The cover 26 and chimneys 27 are removed from the heater 25. Before the evacuation is started the heater 25 is raised to engage the cap 24 and the temperature of the cathode 12 raised to between 300° and 400° C., causing the silver oxide to decompose to finely divided silver. The zirconium oxide is unaffected by this treatment. The finely divided silver is thoroughly mixed with the zirconium oxide.

The vacuum pumping apparatus is started and the liquid air trap 29 is cooled with liquid air. When the pressure has fallen sufficiently the manometer 40 is turned on. The current in the

heater 25 is adjusted to bring the oven temperature up to 400° C. and maintained until the manometer shows a pressure of 5×10^{-5} mm. of Hg (millimeters of mercury) or lower. The current is then turned off and the oven allowed to cool. Slow leaks somewhere in the system are indicated if the pressure is not less than 2×10^{-5} mm. of Hg when the tubes are cooled to room temperature. During this treatment the cathodes 12 are gently heated by induced high frequency current from coil 17 to insure the complete decomposition of the zirconium nitrate. The coil 17 is so positioned as to avoid heating the caesium pellet 14 at this time. These heat treatments remove occluded gases from the tubes but do not cause any chemical reaction in the caesium pellets.

The cathodes 12 are now in condition to be treated with caesium vapor under suitable temperature conditions. A source of high frequency current is connected to the coils 17 in succession to "flash" the caesium capsules, that is, to induce sufficient current in the copper wire 13 and capsule 14 to start a chemical reaction of the ingredients of the caesium pellet. The exothermic reaction which follows develops a large amount of heat and causes the immediate and complete expulsion of all of the caesium. The high frequency source is disconnected as soon as the reaction starts. The caesium travels outwardly from the capsules 14 and is condensed on the glass walls of the bulbs 5. The shield 15 prevents the hot caesium vapor from impinging on the cathode surface. This shield 15 is so shaped that it lies substantially parallel to the magnetic lines of force produced by the high frequency current in the coil 17 and therefore is not heated to any great extent by eddy currents induced therein.

Immediately after the caesium capsule is flashed stem heaters (not shown) are inserted around the stems of tubes 5. Thermocouples are placed against each bulb 5 at the surface opposite the stem to indicate temperatures. The cover 26 with the chimneys 27 is placed on the heater 25 and the whole raised until a chimney 27 surrounds each bulb 5. The stem heaters are turned on first and after two minutes the heater 25 is turned on to quickly bring up the temperature of the convection air currents flowing past the bulbs 5. When the hottest bulb reaches a temperature of 150° C. the heater 25 is regulated to hold this temperature for five minutes. At the end of this five-minute period the heater 25 is again regulated to raise the temperature of the air currents and to quickly bring the temperature of the hottest bulb 5 up to 225° C. The heating is continued and the temperature allowed to gradually rise (but not to exceed 300°) until the leakage, or leak current, drops (indicating a drop in vapor pressure and approaching complete absorption of the caesium) and the sensitivity has reached a proper value.

The sensitivity of tubes 5 may be indicated by the ammeter 58 when connected into the circuit by inserting plug 57 into jack 56 of the circuit of Fig. 3. Each cathode 12 is illuminated by a source of light (not shown). Potentiometer 51 is adjusted to give a voltage of 50 volts as shown on voltmeter 55. Switch 52 is closed. The sensitivity of each tube 5 will be indicated by the ammeter 58 if the corresponding switch 53 is closed in its lower position. The tubes 5 are tested from time to time and the hot air treatment is continued until the photoelectric current tends to decrease. As each tube reaches its proper sensitivity the air current for that tube is cut off. When

all of the tubes have reached the proper sensitivity the chimneys are lowered and the bulbs allowed to cool to room temperature with the pumping apparatus still on.

5 When the bulbs 5 are cool and the pressure is down to 2×10^{-5} mm. of Hg the mercury cut-off 33 is closed and argon is admitted from the gas supply unit 36. The argon is admitted until the pressure as indicated by McLeod gauge 31 assumes a steady state at the desired value, when the tubes are sealed off from the header 20 by sealing off the exhaust tubes 16. The pressure of the argon is dependent upon the amount of gas amplification desired in the completed tube.

10 A suitable pressure is 5×10^{-2} mm. of Hg.

The reduction of the silver oxide may be effected before the electrode assembly is sealed into the bulb 5 by heating the coated cathode plate 12 in an oven to a temperature between 300° and 400° C.

The second specific method of preparing a composite matrix, according to this invention, which is to be described, produces a cathode containing caesium, tin and alumina.

25 This method is analogous to the first specific method hereinbefore described. The nickel cathode 12, suitably roughened, is coated with a suspension of tin and aluminum oxides in water. The ingredients, tin oxide and aluminum oxide, in about equal proportions are thoroughly ground in a ball mill and coated on the roughened cathode surface.

The stem assembly including the coated cathode 12 is sealed into the bulb 5 and four of the assembled tubes are sealed onto the pump station. The reduction of the tin oxide is effected by heating in an atmosphere of hydrogen. In order to obviate blackening of the bulb during this reduction process, the bulbs 5 should be made of lead-free glass, such as "Pyrex" glass.

35 In this second method the tubes are outgassed before the tin oxide is reduced. After the tubes are outgassed and evacuated to a pressure of 2×10^{-5} mm. Hg or less, the mercury cut-off 33 is closed and hydrogen is admitted from the gas supply unit 35 to a pressure of 2.5 mm. of Hg as shown by McLeod gauge 30. This pressure, however, is not critical. The heater 25, without the cover 26 and chimneys 27, is raised around the tubes and the temperature brought up to approximately 200° C. to effect the reduction of the tin oxide. Finely divided metallic tin resulting from this reduction process is thoroughly mixed with the aluminum oxide which is unaffected by this heat treatment. The mercury cut-off 33 is now opened and the tubes evacuated to a pressure of 2×10^{-5} mm. of Hg when cool.

Caesium from capsule 14 is next introduced and the sensitizing process completed in the manner hereinbefore specifically described. Care should be taken not to overheat the cathode because metallic tin melts at a temperature in the neighborhood of 232° C. Argon gas may be admitted, as hereinbefore described.

65 This second specific method may be modified by effecting the reduction of the tin oxide in hydrogen before sealing the stem assembly into the bulb 5. In this event, ordinary lead glass may be used for the bulbs 5. Care must be taken, however, not to overheat the cathodes 12 in the outgassing process or any subsequent steps of the process because of the relatively low melting point of metallic tin.

The third specific method of preparing a composite matrix, according to this invention, which

is to be described, produces a cathode containing caesium, copper and aluminum silicate. This method is also analogous to the specific methods hereinbefore described. A suitably roughened nickel cathode 12 is coated with a suspension of cupric oxide and aluminum silicate in water. The ingredients, cupric oxide and aluminum silicate, in proportions of about 1 to 4 are thoroughly ground together in a ball mill before being sprayed on the cathode 12.

The cupric oxide is reduced by heating in an atmosphere of hydrogen to a temperature of 400° C. If the reduction is effected before the stem assembly is sealed into the bulb 5, ordinary lead glass may be used for the bulb, otherwise the bulb should be made of lead-free glass as set forth in the description of the second specific method. Since metallic copper melts at a temperature in the neighborhood of 1083° C., the outgassing and sensitizing processes may be carried out at the temperatures specified for the first described specific process. The method of introducing caesium and argon is identical with that hereinbefore described.

Small amounts of zirconium nitrate may also be used in the second and third methods as a binder. If used, care must be taken to insure that it is completely decomposed before the caesium is admitted.

Others of the alkali metals may be used in place of the caesium of the herein described methods. Such other alkali metals are potassium, sodium, rubidium and lithium.

Silver, tin or copper oxides may be used with zirconium or aluminum oxides or aluminum silicate.

The three specific methods herein described appear at present to be preferred but the other methods mentioned are entirely feasible and produce good electron emitting surfaces which are sensitive to visible light.

The first specifically described method produces a photoelectric tube having an anode and a cathode within a glass container filled with argon at low pressure, which cathode comprises a nickel plate having a roughened surface carrying a composite matrix of an intimate mixture of finely divided caesium, metallic silver and zirconium oxide, whose exposed surface contains free caesium. The caesium is so finely divided that the particles approach atomic dimensions so that the behavior of an atom will depend more upon the other ingredients in the matrix than upon the neighboring atoms of caesium. The cathode, therefore, may be said to comprise a mixture of finely divided zirconium oxide and metallic silver throughout which mixture is adsorbed free caesium. Some of the caesium also may well be alloyed or absorbed in the free silver particles.

The second specifically described method produces a similar photoelectric tube having a matrix of an intimate mixture of finely divided caesium, metallic tin and aluminum oxide.

The third specifically described method also produces a similar photoelectric tube having a matrix of an intimate mixture of finely divided caesium, metallic copper and aluminum silicate.

The other suggested methods produce similar photoelectric tubes having matrices comprising specifically different ingredients.

What is claimed is:

1. The process of forming an electron emitting cathode in an evacuated container, comprising depositing a layer of a mixture of an easily reduc-

- ible metallic compound and a refractory compound which is stable with respect to the atmosphere upon a substratum, reducing one of the compounds in said mixture by a process including heating to a temperature above that which reduces said metallic compound and below that which reduces said refractory compound leaving metallic particles distributed throughout the refractory compound, and applying an alkali metal to the resulting mixture in the presence of heat.
2. The method of producing an electron emissive cathode which comprises providing a coating of a mixture of an easily reducible metallic oxide and a refractory oxide which is stable with respect to the atmosphere on a metallic support within a container, reducing only the easily reducible oxide leaving the refractory oxide unchanged to form metallic particles distributed through the refractory oxide, introducing an alkali metal vapor into the container, and heating the resulting layer to cause the alkali metal to penetrate said layer.
3. The method of producing an electron emissive cathode which comprises providing a coating of a mixture of an easily reducible oxide and a refractory compound which is stable with respect to the atmosphere on a metallic support, mounting said coated support within a container, reducing said oxide including heating to a temperature above that which reduces said easily reducible oxide and below that which reduces said refractory compound to form metallic particles distributed throughout the refractory compound, outgassing and evacuating said container, and subjecting said resulting coating to alkali metal vapor and heat to cause the alkali metal to penetrate the coating.
4. The method of producing an electron emissive cathode which comprises providing a coating of a mixture of silver oxide and zirconium oxide on a support within a container, heating said layer to reduce the silver oxide only to metallic silver, introducing an alkali metal vapor into said container, and heating the resulting layer in the presence of said vapor to cause the alkali metal to penetrate said layer.
5. The method of producing an electron emissive cathode which comprises providing a coating of a mixture of tin oxide and aluminum oxide on a support within a container, heating said layer in the presence of hydrogen to reduce said tin oxide to metallic tin, introducing an alkali metal vapor into said container, and heating the resulting layer in the presence of said vapor to cause the alkali metal to penetrate said layer.
6. The method of producing an electron emissive cathode which comprises providing a coating of a mixture of copper oxide and aluminum silicate on a support within a container, heating said layer in the presence of hydrogen to reduce said copper oxide to metallic copper, introducing an alkali metal vapor into said container, and heating the resulting layer in the presence of said vapor to cause the alkali metal to penetrate said layer.
7. A photoelectric cathode comprising a support within an evacuated container, and a layer on said support of an intimate mixture of finely divided alkali metal, silver, and zirconium oxide.
8. A photoelectric cathode comprising a support within a container and a layer on said support of an intimate mixture of finely divided caesium, silver, and zirconium oxide.
9. A photoelectric cathode comprising a support within an evacuated container and a layer on said support of an intimate mixture of finely divided alkali metal, tin, and aluminum oxide.
10. A photoelectric cathode comprising a support within an evacuated container and a layer on said support of an intimate mixture of finely divided caesium, tin, and aluminum oxide.
11. A photoelectric cathode comprising a support within an evacuated container and a layer on said support of an intimate mixture of finely divided alkali metal, copper, and metallic silicate.
12. A photoelectric cathode comprising a support within an evacuated container and a layer on said support of an intimate mixture of finely divided alkali metal, copper, and aluminum silicate.
13. A photoelectric cathode comprising a support within an evacuated container and a layer on said support of an intimate mixture of finely divided caesium, copper, and aluminum silicate.
14. A photoelectric tube comprising an evacuated container and an anode and a cathode mounted therein, said cathode comprising a metallic support, and a layer on said support of an intimate mixture of finely divided caesium, silver, and zirconium oxide.
15. A photoelectric tube comprising an evacuated container and an anode and a cathode mounted therein, said cathode comprising a metallic support, and a layer on said support of an intimate mixture of finely divided caesium, silver, zirconium, and zirconium oxide.
16. The method of producing an electron emissive cathode which comprises providing a layer of a mixture of a metallic oxide and a refractory compound upon a substratum, heating said mixture in the presence of hydrogen to reduce said oxide to the metal thereof, and applying an alkali metal to the resulting layer by heating causing the alkali metal to penetrate said layer.
17. A photoelectric cathode comprising a support within an evacuated container and a layer on said support of an intimate mixture of finely divided alkali metal, fine particles of a metal having a melting point higher than that of the alkali metals, and fine particles of an insoluble metal oxygen refractory which is stable with respect to the atmosphere.
18. A photoelectric cathode comprising a support within an evacuated container and a layer on said support of an intimate mixture of finely divided alkali metal, fine particles of a metal having a melting point higher than that of the alkali metals, and fine particles of an insoluble refractory oxide which is stable with respect to the atmosphere.
19. The method of producing an electron emissive cathode which comprises providing a layer of a mixture of an oxide of a base metal and a refractory compound upon a substratum, heating said mixture in a reducing atmosphere to reduce said oxide to the metal thereof, and applying an alkali metal to the resulting layer by heating, causing the alkali metal to penetrate said layer.