Nov. 6, 1951 A. SOMMER 2,574,356

PROCESS OF MAKING PHOTOELECTRIC CATHODES

Filed March 1, 1948

Fig. 1.

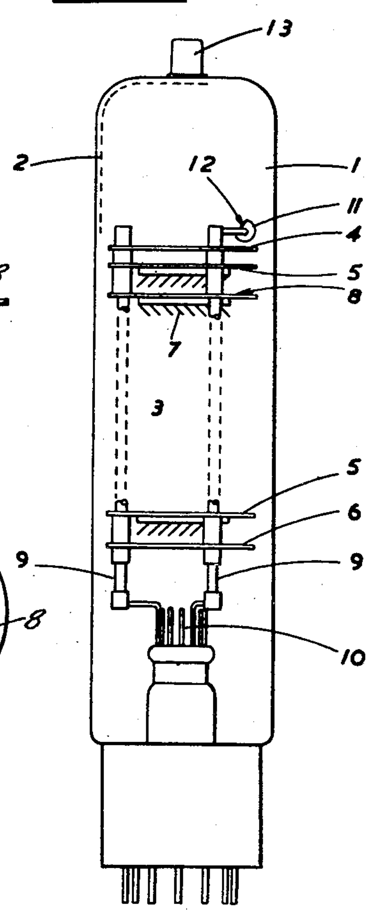
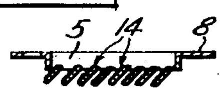


Fig. 2.



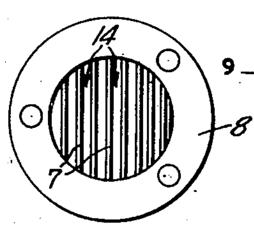


Fig. 3.

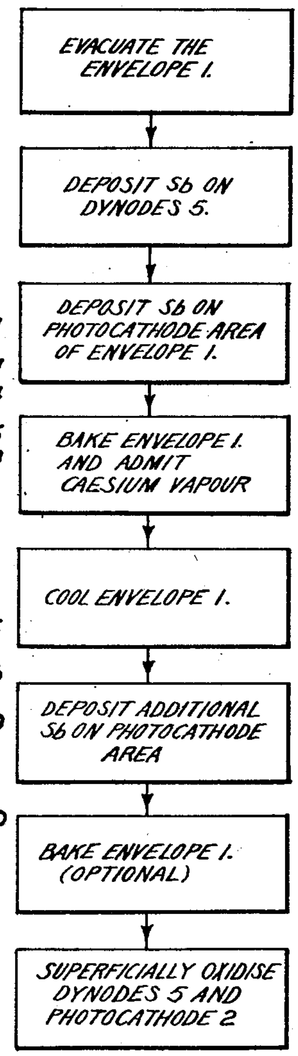


Fig. 4.

Inventor:
Alfred Sommer
By J. O. Ollier
Attorney

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PROCESS OF MAKING PHOTOELECTRIC CATHODES

Alfred Sommer, Iver, England, assignor to Electric & Musical Industries Limited, Hayes, England, a company of Great Britain

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This invention relates to electron discharge devices of the kind having an electrode sensitised to be an emitter of photo-electrons or secondary electrons (referred to hereinafter generically as impact electrons) under the impact of photons or bombarding electrons. Devices of this kind are hereinafter referred to as of the kind described. The invention relates especially but not exclusively to photo-electric devices incorporating electron multiplying electrodes (or so-called dynodes).

A photo-electric device has been proposed comprising a photo-electric cathode deposited on the envelope of the device and having a number of nickel dynodes within the envelope, the photo-cathode and the dyn. des each comprising a layer of antimony and caesium, caesium being introduced after the antimony has been deposited and the device being baked during and after the introduction of the caesium in order to cause the caesium to react with the antimony. However, it is found that with such photo-electric devices the final sensitivity of the photo-cathode when the device has cooled has a low value in comparison with the sensitivity when the device is hot and also in comparison with the sensitivity obtained in photo-electric devices having similar photo-cathodes but not incorporating dynodes. As a result of experiment, it appears to the applicant that the reduction of sensitivity is probably due to the fact that after the aforesaid baking operation the glass envelope cools much more rapidly than the dynodes and because of the temperature difference so established, any excess caesium in the tube is deposited preferentially on the photo-cathode with the result that the quantity of caesium on the latter may be raised above the quantity required for optimum photo-sensitivity, said quantity being fairly critical.

A similar effect may arise in other electron discharge devices and the present invention therefore has general application to such devices, and the object of the present invention is to reduce or nullify the resultant loss of sensitivity.

In accordance with the present invention there is provided a method of manufacturing electron discharge devices of the kind described wherein said electrode comprises a photo-electrically active substance and a metal which have been caused to react by heating said device and wherein a loss of sensitivity of said electrode on cooling the device relative to the sensitivity before cooling is nullified or substantially reduced by depositing on said electrode an additional quantity

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of metal which will react with said photo-electrically active substance.

In further accordance with the present invention there is provided a method of manufacturing an electron discharge device of the kind described wherein said electrode comprises a photo-cathode provided on the envelope of the device and the device comprises at least one dynode within the envelope, said cathode and said dynode each comprising a photo-electrically active substance and a metal which have been caused to react by heating said device, and wherein a loss of sensitivity of said cathode on cooling the device relative to the sensitivity before cooling is nullified or substantially reduced by depositing on said cathode an additional quantity of metal which will react with said photo-electrically active substance.

In order that the invention may be clearly understood and readily carried into effect, it will now be more fully described with reference to the accompanying drawing whereon Figure 1 diagrammatically illustrates a photo-electric device manufactured by a method according to one example of the invention, Figure 2 is a cross-sectional elevation, on an enlarged scale, of a dynode employed in the device illustrated in Figure 1, Figure 3 is a plan view of Figure 2, and Figure 4 is a flow diagram illustrating the process of manufacture.

Referring to the drawing, the device comprises a highly evacuated glass envelope 1 having a photo-electric cathode 2 comprising a coating of antimony and caesium on the inner surface of the envelope at one end thereof, and an electrode assembly 3 comprising a focussing electrode 4, a plurality of dynodes 5 and a collecting electrode 6, the electrodes 4, 5 and 6 being arranged at intervals along the axis of the device. The focussing electrode 4 comprises a flat ring while the collecting electrode comprises a flat disc. The dynodes 5 are all similar and therefore some have been omitted for convenience of illustration and, as shown in Figures 2 and 3, each comprises a coating 14 of antimony and caesium provided on a set of nickel louvres 7 attached at their ends to a centrally apertured nickel flange 8. The electrodes 4, 5 and 6 are supported in spaced relationship by insulating pillars 9 attached at their lower ends to certain of the lead-in pins 10 of the device. One of the pillars 9 also supports at its upper end a container 11 from which the antimony utilised to form the photo-cathode 2 is evaporated during the manufacture of the device, the container 11 having an aperture 12 facing the surface where the photo-cathode is formed. The lead-in pins 10 are electrically connected in known manner to the electrodes 4, 5 and 6, and also to a small tungsten coil in the container 11 so that a current can be passed through said coil when it is desired to evaporate antimony from the container, the connections being however omitted in the drawing for convenience of illustration. The photo-cathode 2 is electrically connected to a contact 13 at the top of the envelope 1.

The process of manufacture of the device is illustrated in Figure 4 and according thereto, after positioning the assembly 3 in the envelope 1, evacuating said envelope and providing a layer of antimony (denoted by the symbol Sb in Figure 4) on the louvres 7, current is passed through the coil in the container 11 so as to cause evaporation of antimony from a pellet thereof which has previously been provided in said container, the evaporated antimony being deposited on the area of the envelope surface where it is desired to form the photo-cathode. When the required quantity of antimony has been deposited the current supplied to the coil in the container 11 is switched off so as to discontinue the evaporation, and subsequently, while baking the device at a temperature between 150° C. and 200° C. caesium is distilled into the envelope from a side tube to cause it to react with the antimony of the photo-cathode 2 and the dynodes 5, the result of the reaction being it is believed the formation of an intermetallic compound or alloy of the antimony and caesium. The optimum proportion of caesium to antimony has been found to be about three atoms of caesium to one atom of antimony, that is, the caesium and antimony are present in the compound in substantially stoichiometric proportions. However, during the distillation of the caesium, some caesium is inevitably deposited on other parts of the device than the surfaces of the electrodes which it is desired to sensitise and particularly on the marginal flanges 8 of the dynodes, and therefore the quantity of caesium introduced is in excess of that required to give the desired proportion. If desired, the flanges 8 may be coated with a material which will absorb caesium such as colloidal-graphite. After introducing the caesium the baking is continued for about 10 minutes, as much as possible of the excess caesium being removed by pumping. The device is thereafter allowed to cool to room temperature and it can be observed that the photoelectric sensitivity of the photo-cathode 2 falls during the cooling of the device and eventually when the device is cool is only a fraction of the sensitivity at the baking temperature. After the device is cool an additional very small quantity of antimony is evaporated on to the photo-cathode 2 from the container 11 by passing a current through the coil therein, sufficient antimony being of course provided in the container 11 originally to allow for this further evaporation. The deposition of this additional quantity of antimony on the photo-cathode 2 causes an increase in the sensitivity of the photo-cathode, the quantity required being determined experimentally so as to obtain the maximum sensitivity. The device may if desired be baked for a short time after the additional antimony has been deposited, superficial oxidation of the photo-cathode 2 and the dynodes 5 being thereafter effected in known manner.

Devices manufactured in accordance with the above described example of the invention have been found to have photo-cathodes with sensitivities of the order of 50 microamperes per lumen of incident light (μa./l.), compared with sensitivities of the order of 20 μa./l. without deposition of the additional antimony on the photo-cathode after cooling. During operation of the device potentials are applied to the electrodes so that in known manner electrons released by light incident upon the photo-cathode 2 are accelerated to the nearest dynode 5 where they release a number of secondary electrons greater than the number of incident primary electrons, the secondary electrons being accelerated to the next dynode 5 and so on, the electrons being ultimately collected by the collecting electrode 6.

It will be understood that the invention is not limited to electron discharge devices employing photo-electric or secondary-electron emitting electrodes which comprise antimony and caesium since other photo-electrically active substances such as the other alkali metals can be used instead of caesium, and other metals, for example bismuth, which react with the photo-electrically active substances can be used instead of antimony.

What I claim is:

1. A method of producing an electron discharge device sensitized to be an emitter of impact electrons, including the steps of depositing metal which reacts with alkali metals on a supporting surface, exposing the metal deposit on said surface to an alkali metal and heating said surface to cause said first metal and said alkali metal to react, cooling said surface, and thereafter depositing on said surface additional metal which reacts with alkali metals to reduce loss of sensitivity on cooling by the emissive coating on said surface.

2. A method of producing an electron discharge device sensitized to be an emitter of impact electrons, including the steps of depositing metal which forms an intermetallic compound with caesium on a supporting surface, exposing the metal deposit on said surface to caesium vapour and heating said surface to cause said first metal and said caesium to react to form an intermetallic compound, cooling said surface, and thereafter depositing on said surface additional metal which forms an intermetallic compound with caesium to reduce loss of sensitivity on cooling by the emissive coating on said surface.

3. A method for producing an electron discharge device sensitized to be an emitter of impact electrons, including the steps of depositing metal selected from the group consisting of antimony and bismuth on a supporting surface, exposing the metal deposit on said surface to caesium vapour and heating said surface to cause said first metal and said caesium to react to form an intermetallic compound, cooling said surface, and thereafter depositing on said surface additional metal selected from said group to reduce loss of sensitivity on cooling by the emissive coating on said surface.

4. A method of producing an electron discharge device sensitized to be an emitter of impact electrons, including the steps of depositing metal which reacts with alkali metals on a supporting surface, exposing the metal deposit on said surface to an alkali metal and heating said surface to cause said first metal and said alkali metal to react, cooling said supporting surface, and thereafter depositing on said supporting surface additional metal which reacts with alkali metals to cause said additional metal to react

with free alkali metal present on said supporting surface after cooling thereof, whereby loss of sensitivity by the emissive coating formed on said supporting surface due to the presence of free alkali metal thereon is substantially reduced.

5. A method of producing an electron discharge device sensitized to be an emitter of impact electrons, including the steps of depositing metal which forms an intermetallic compound with caesium on a supporting surface, exposing the metal deposit on said surface to caesium vapour and heating said surface to cause said first metal and said caesium to react to form an intermetallic compound, cooling said supporting surface, and thereafter depositing on said surface additional metal which reacts with caesium to cause said additional metal to react with free caesium present on said supporting surface after cooling thereof, whereby loss of sensitivity by the emissive coating formed on said supporting surface due to the presence of free caesium thereon is substantially reduced.

6. A method of producing an electron discharge device sensitized to be an emitter of impact electrons, including the steps of depositing metal selected from the group consisting of antimony and bismuth on a supporting surface, exposing the metal deposit on said surface to caesium vapour and heating said surface to cause said first metal and said caesium to react to form an intermetallic compound, cooling said supporting surface, and thereafter depositing on said supporting surface additional metal selected from the group consisting of antimony and bismuth to cause said additional metal to react with free caesium present on said supporting surface after cooling thereof, whereby loss of sensitivity by the emissive coating formed on said supporting surface due to the presence of free caesium thereon is substantially reduced.

7. A method of producing a photoelectric cell of the multiplier type comprising a photocathode on part of the inner surface of the envelope of the device and at least one dynode within the envelope, including the steps of depositing metal which reacts with alkali metal on part of the inner surface of the envelope, depositing metal on a metallic support before depositing alkali metal on said envelope surface and said support within said envelope, thereafter exposing the deposits to alkali metal and heating the envelope to cause the metal deposited on the envelope surface and on the metallic support to react with the alkali metal, and thereafter cooling said envelope and depositing additional metal which reacts with alkali metal on said part of the envelope surface to reduce loss of sensitivity upon cooling by the photocathode on the envelope surface.

8. A method of producing a photoelectric cell of the multiplier type comprising a photocathode on part of the inner surface of the envelope of the device and at least one dynode within the envelope, including the steps of depositing metal which forms an intermetallic compound with caesium on part of the inner surface of the envelope, depositing the same kind of metal on a metallic support within said envelope, exposing the deposits on the envelope surface and on the metallic support to caesium vapour and heating the envelope to cause the caesium to react with the deposits to form an intermetallic compound therewith, cooling said envelope, and thereafter depositing additional metal which forms an intermetallic compound with caesium on said part of the envelope surface to reduce loss of sensitivity upon cooling by the photocathode formed on the envelope surface.

9. A method of producing a photoelectric cell of the multiplier type comprising a photocathode on part of the inner surface of the envelope of the device and at least one dynode within the envelope, including the steps of depositing metal selected from the group consisting of antimony and bismuth on part of the inner surface of the envelope, depositing the same kind of metal on a metallic support within said envelope, exposing the deposits to caesium vapour and heating the envelope to cause the deposited metal and the caesium to react to form an intermetallic compound, cooling said envelope, and thereafter depositing additional metal selected from said group on said part of the envelope surface to reduce loss of sensitivity upon cooling by the photocathode formed on the envelope surface.

10. A method of producing a photoelectric cell of the multiplier type comprising a photocathode on part of the inner surface of the envelope of the device and at least one dynode within the envelope, including the steps of depositing metal selected from the group consisting of antimony and bismuth on part of the inner surface of the envelope, depositing the same kind of metal on a metallic support within said envelope, exposing the deposits to caesium vapour and heating the envelope to cause the deposited metal and the caesium to react, cooling said envelope, and thereafter depositing an additional quantity of said first metal on said part of the envelope surface until said first metal and the caesium are present on said support in substantially stoichiometric proportions.

11. A method of producing a photoelectric cell of the multiplier type comprising a photocathode on part of the inner surface of the envelope of the device and at least one dynode within the envelope, including the steps of evaporating antimony to form layers thereof on part of the inner surface of the envelope and on a metallic support, exposing said layers of antimony to caesium vapour and heating the envelope to cause the antimony on said layers to react with caesium to form an intermetallic compound therewith, cooling the envelope, and thereafter evaporating additional antimony onto said part of the envelope surface to react with free caesium present thereon after cooling of the envelope, whereby loss of sensitivity by the photocathode formed on said part of the envelope surface due to the presence of free caesium thereon is substantially reduced.

12. A method of producing an electron discharge device sensitized to be an emitter of impact electrons, including the steps of depositing metal selected from the group consisting of antimony and bismuth on a supporting surface, exposing the metal deposit on said supporting surface to caesium vapor and heating said supporting surface to cause said first metal and said caesium to react, cooling said supporting surface, and thereafter depositing on said supporting surface an additional quantity of said first metal until said first metal and said caesium are present on said surface in substantially stoichiometric proportions.

13. A method of producting an electron discharge device sensitized to be an emitter of impact electrons, including the steps of depositing metal which reacts with alkali metals on a sup-

porting surface before depositing alkali metal on said surface, thereafter exposing the metal deposit on said surface to an alkali metal and heating said surface to cause said first metal and said alkali metal to react, and thereafter cooling said supporting surface and depositing on said supporting surface additional metal which reacts with alkali metals to reduce loss of sensitivity on cooling by the emissive coating on said supporting surface.

14. A method of producing an electron discharge device sensitized to be an emitter of impact electrons, including the steps of depositing a metal selected from the group consisting of antimony and bismuth on a supporting surface before depositing caesium on said surface, thereafter exposing the metal deposit on said surface to caesium and heating said surface to cause said first metal and said caesium to react, and there-

after cooling said supporting surface and depositing on said supporting surface additional metal selected from said group to reduce loss of sensitivity on cooling by the emissive coating on said supporting surface.

ALFRED SOMMER.

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