March 20, 1956 A. H. SOMMER 2,739,084

SECONDARY ELECTRON EMITTING COATINGS
AND METHOD FOR PRODUCING SAME
Filed April 15, 1952

FIG. 1.

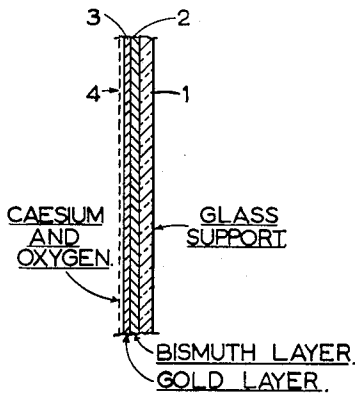


FIG. 2.

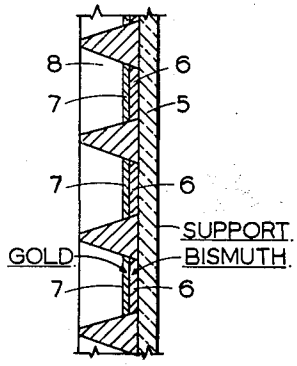


FIG. 3.

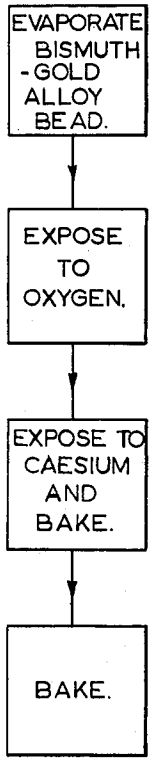
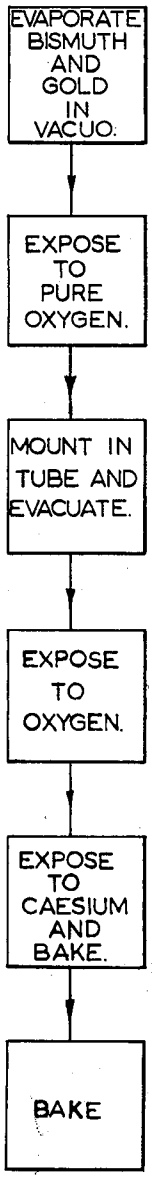


FIG. 4.



Inventor
A. H. Sommer
By Glascock Downing & Seebold
Attys.

United States Patent Office 2,739,084
Patented Mar. 20, 1956

2,739,084

SECONDARY ELECTRON EMITTING COATINGS AND METHOD FOR PRODUCING SAME

Alfred Hermann Sommer, Iver, England, assignor to Electric & Musical Industries Limited, Hayes, England, a British company

Application April 15, 1952, Serial No. 282,314

Claims priority, application Great Britain April 28, 1951

4 Claims. (Cl. 117—211)

This invention relates to electrodes which are capable of emitting electrons when exposed to light.

Such electrodes may be required as photo-sensitive cathodes in photo-electric cells and television pick-up tubes or as mosaic screens in television pick-up tubes, and it has been proposed hitherto to form such electrodes by applying to a suitable support an alloy consisting of caesium or other alkali metal and antimony or bismuth. However, in the case of electrodes formed of antimony and caesium, the red response of the electrode is poor whilst electrodes formed of bismuth and caesium have a low sensitivity.

The object of the present invention is to provide an improved electrode capable of emitting electrons when exposed to light, with a view to combining good sensitivity with a desirable colour response.

A further object of the present invention is to provide an electrode which is capable of emitting electrons when exposed to light and whereon the emissive material comprises bismuth, gold, oxygen and an alkali metal.

A further object of the present invention is to provide an improved method of manufacturing an electrode which is capable of emitting electrons when exposed to light, wherein bismuth and gold are deposited on to a supporting surface by evaporation from an alloy of bismuth and gold, and the bismuth and gold deposited on said supporting surface are exposed to oxygen and an alkali metal so as to form said electrode. This method has the advantage that, although involving only a single evaporation step, it provides an electrode in which the bismuth is deposited mainly under the gold, which has been found to be desirable.

In order that the said invention may be clearly understood and readily carried into effect, the same will now be more fully described with reference to the accompanying drawings, in which:

Figure 1 illustrates one example of the present invention applied to a photo-cathode for use in a television pick-up tube, and

Figure 2 illustrates another example of the present invention applied to a mosaic screen for use in a television pick-up tube.

Figure 3 is a flow diagram of one process of manufacturing a photo-cathode in accordance with the present invention.

Figure 4 is a flow diagram of one process of manufacturing a mosaic screen in accordance with the present invention.

The photo-cathode illustrated in Figure 1 comprises a transparent insulating support **1** of glass or other suitable material having a thin layer of bismuth **2** deposited on one surface thereof and a thin layer of gold **3** deposited on the bismuth. The composite bismuth and gold coating **2**, **3** is sensitised by oxygen and caesium indicated by the dotted line **4**. An electrode of this construction can be manufactured, for example, by the following process. The bismuth layer **2** is first deposited on the support **1** by evaporation in vacuo from a bismuth bead until the light transmission of the support **1** is reduced to about 50 per cent, the support **1** being as aforesaid transparent. Thereafter the gold layer **3** is deposited by evaporation on top of the bismuth layer from a gold bead and this evaporation is continued until the light transmission of the gold and bismuth layers has dropped to about 40 per cent. The composite gold and bismuth surface is then exposed to oxygen, if desired by exposing it to a discharge in oxygen. When oxidation occurs the light transmission of the layers **2** and **3** increases and the oxidation is continued until the light transmission becomes constant, which occurs when the light transmission is of the order of 50 per cent. The oxygen is believed only to affect the bismuth. Thereafter the layers **2** and **3** are exposed to caesium vapour, while being baked at a temperature of about 150° C., the caesiation being carried out in conventional manner while observing the photo-electric sensitivity of the layers **2** and **3** and being discontinued when the sensitivity passes the maximum value. Thereafter further baking is carried out with the object of removing excess caesium from the layers **2** and **3**.

Instead of manufacturing the electrode by evaporating the bismuth and gold from separate beads as above described, alternatively and with advantage, bismuth and gold can be evaporated from a composite bead consisting of an alloy containing about two parts of bismuth to one part of gold. The process thus modified is illustrated by the flow diagram of Figure 3. In this case, when the bead is heated, the bismuth evaporates first due to its lower evaporation temperature followed by the gold so that the bismuth is mainly deposited, as the layer **2** under the gold layer **3**. The weight of the bead is predetermined to give the required thicknesses of the layers **2** and **3** on the transparent support **1** when the entire bead has been evaporated, variations in light transmission being again employed as an indication of the thickness during the initial step of predetermining the required weight of bead.

Electrodes such as described with reference to Figure 1 have been found to have sensitivities exceeding 50 μ A./L. when employed as photo-cathodes, and their red response is such as to render them eminently suitable for use in television pick-up tubes. A further improvement in sensitivity may in some cases be obtained with a superficial oxidation of the electrode after the exposure to caesium.

Figure 2 illustrates a fragment of a mosaic screen for use in a television pick-up tube, and it comprises a transparent support **5**, on which are provided photo-electrically sensitised mosaic elements. Three such elements are shown and they each comprise bismuth **6** and gold **7** sensitised with oxygen and caesium as described with reference to Figure 1 the bismuth **6** again being disposed mainly under the gold. In order to manufacture such a mosaic screen **2** a metal mesh **8** (only a fragment of which is shown) is mounted with one of its surfaces in close contact with that surface of support **5** on which the mosaic elements are to be provided. The filaments of the mesh are of substantially triangular cross-section and the mesh is applied to the support **5** with the bases of the filaments against the support. Thereafter the bismuth and gold are deposited by either of the methods described with reference to Figure 1, the mesh confining the evaporated metal as it is deposited on the support **5** to discrete areas thereof in well known manner. Thereafter the mesh **8** is removed and sensitisation of the mosaic elements with oxygen and caesium is effected.

An advantage which arises from the invention is that the bismuth and gold can be deposited on the support and thereafter exposed to air without significantly affecting the properties of the electrode finally produced. For example in the manufacture of a photo-electric cell, bismuth and gold to form a photo-cathode in accordance with the

invention can be provided on a wall of the tube, which in this case constitutes the support 1, before mounting other electrodes in the tube, thereby considerably simplifying the manufacture of the photo-cell. In such a case although it has been found that the exposure to air, which inevitably occurs when mounting the other electrodes in the tube, has no significant harmful effect, it is considered advantageous to expose the deposited bismuth and gold to pure oxygen prior to the exposure to air since it is thought that the oxygen forms a protecting oxide layer which reduces the tendency of the deposited metal to absorb sulphur from the atmosphere. After the tube 5 has been finally exhausted of air, the tube is baked to a temperature of the order of 300° C. and is then given a further exposure to oxygen. Caesiation and further oxidation if desired are then carried out in the normal manner for example as described above with reference to Figure 1. This process is illustrated by the flow diagram of Figure 4. In a similar manner, if a mosaic screen for a television pick-up tube is required, bismuth and gold to form the mosaic elements can be deposited on the support 5 (Figure 2) before mounting the support in the pick-up tube.

The invention has been described above with reference to the manufacture of partially transparent electrodes intended for use in such manner that the light is transmitted through the electrode to the electron emissive surface thereof. It is to be understood, however, that the invention can be applied to the manufacture of electrodes intended for use where the light is projected directly on the electron emissive surface of the electrode, in which case thicker metallic layers can be employed. Moreover, the electrodes in accordance with the invention may be produced by a process in which the exposure of oxygen and caesium occurs after only the bismuth has been deposited, in this case gold being deposited after the exposure to oxygen and caesium. Although the advantages of the present invention arise mainly when the electrode is used as a photo-cathode or mosaic screen, electrodes

such as described above are also capable of being used with advantage as secondary electron emitting electrodes.

What I claim is:

1. An electrode capable of emitting electrons when exposed to light, said electrode comprising a support and emissive material thereon comprising bismuth, gold, oxygen and an alkali metal, and containing about two parts of bismuth to one part of gold.

2. A method of manufacturing an electrode capable of emitting electrons when exposed to light, said method comprising the steps of evaporating an alloy body containing about two parts of bismuth and one part of gold to deposit bismuth and gold on a supporting surface, and exposing the bismuth and gold deposited on said supporting surface to oxygen and an alkali metal.

3. A method of manufacturing an electrode capable of emitting electrons when exposed to light, said method comprising the steps of evaporating an alloy body consisting of about two parts of bismuth to one part of gold to deposit bismuth and gold on a supporting surface, exposing the bismuth and gold deposited on said supporting surface to oxygen and an alkali metal until the photoelectric sensitivity has passed the maximum value, and thereafter baking the support to remove excess alkali metal therefrom.

4. A method according to claim 2, including the steps of exposing the bismuth and gold to air after deposition on said supporting surface, and exposing the bismuth and gold to oxygen before and after said exposure to air and before exposure to the alkali metal.

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