June 4, 1935. J. H. DE BOER ET AL 2,003,344

PHOTO-ELECTRIC TUBE

Filed May 15, 1930

Fig. 1

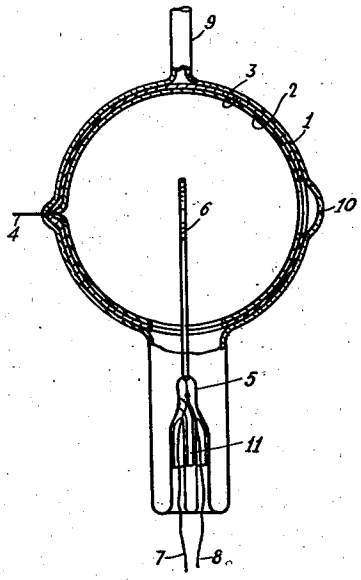
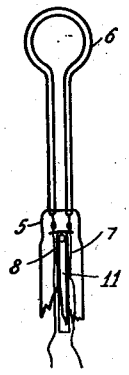


Fig. 2



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PHOTO-ELECTRIC TUBE

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11 Claims. (Cl. 250—27.5)

The invention relates to photoelectric tubes, and more particularly to that type of photoelectric tubes which comprises an electrode containing a photo-active substance which on being subjected to radiation emits electrons, the number of which depends on the intensity of the radiation.

The applicants already have previously proposed to provide between the photo-active substance and a supporting surface or substratum carrying the photo-active electrode, an intermediate layer containing a chemical compound which is preferably so chosen that the photo-active substance is better adsorbed by the intermediate layer than by the substratum. The chemical compound may advantageously consist of an oxide or a halide, for example of calcium fluoride.

Now the applicants have found that the value of the electric resistance of such a photo-active electrode may be very high, which is not favorable for the sensitiveness of the tube. The invention has for its object to obviate this disadvantage and to decrease the resistance of the photo-active electrode.

In a photoelectric tube according to the invention, the photo-active substance, constituted, for example, by cesium, is provided on an intermediate layer which contains a chemical compound and electrically conducting particles. The electric resistance of such an electrode is considerably smaller than that of an electrode in which the intermediate layer has no conducting particles. Conveniently, these particles may be constituted by particles of the photo-active substance which for this purpose may be caused to penetrate into the intermediate layer owing to which at the same time the emission of electrons is increased. This seems to result therefrom that electrons are also liberated in the electrode by the light falling through it.

The penetration of the photo-active substance into the intermediate layer may be effected by heating the tube which has been closed after photo-active material has been provided on the intermediate layer. The penetration of the photo-active substance into the intermediate layer may be facilitated by causing this layer to contain particles of another conducting material. Besides, the resistance of the photo-active electrode may be diminished furthermore by these conductive particles.

The intermediate layer utilized in accordance with the invention may be formed in different ways. The chemical compound and the conducting particles may be applied to the substratum by simultaneously evaporating this compound and a conducting material. These substances may be provided in the tube, for example on an electrode. The intermediate layer should preferably be formed by a chemical reaction, in which event the reactive substances may be provided, by evaporation, on the substratum. In this case the reaction may advantageously be started with a difficultly volatile metal which is heated in the tube, preferably in a vacuum, together with a chemical compound of a readily volatile metal and a negative constituent capable of forming with the difficultly volatile metal a readily volatile compound. In this case, the starting materials to be utilized are so chosen that the evaporating substances react with each other so that the starting materials are formed again, at least partly, on the substratum in a finely divided and thoroughly mixed state. To the mixture, which is to be heated in the tube, may also be added another substance which facilitates the chemical reaction or partly produces other products.

It is also possible to provide the chemical compound present in the intermediate layer and the photo-active substance, and if desired also other conducting particles, simultaneously on the substratum. For this purpose the photo-active substance may be advantageously developed in the tube or in a space connected thereto by heating a mixture containing a compound of the photo-active substance, for example cesium chromate, and a reducing agent, for example, zirconium. In addition, the mixture may contain a chemical compound, for example, sodium-fluoride, which evaporates during the heating or reacts with the reducing agent in the manner described in the preceding paragraph.

The invention will be described more fully with reference to the accompanying drawing which represents diagrammatically, by way of example, a photoelectric tube according to the invention. In the drawing:

Figure 1 is a section of a photoelectric tube; and

Figure 2 shows a detail thereof.

The photoelectric tube illustrated has a wall 1 consisting, for example, of glass, to which is applied a layer 2 of photo-active material, for example of alkalimetal. However, instead of being applied directly to the wall of the tube, the layer 2 is applied to an intermediate layer 3 which contains a chemical compound, for example, calcium fluoride, and conducting particles. The

photo-active electrode is connected to a supply wire 4 which is taken out through the wall of the tube. On the stem 5 of the photoelectric tube is arranged an electrode 6, which, as distinctly appears from Figure 2, has the shape of a nearly closed ring and which is connected to supply wires 7 and 8.

A method is hereinafter described, with the aid of which the intermediate layer 3 can be formed and the conducting particles may be provided in the intermediate layer so as to have a finely divided form and to be thoroughly mixed with the chemical compound. Prior to the arrangement of the electrode 6 in the tube, this electrode is coated with a mixture containing a difficultly volatile metal and a compound of a readily volatile metal with another ingredient capable of forming with the difficultly volatile metal a readily volatile compound. The mixture may contain, for example, tungsten and calcium fluoride. After the tube has been exhausted, the mixture provided on the electrode 6 is heated, which may be effected by causing, with the aid of the supply wires 7 and 8, a heating current to pass through the electrode 6. Due to this heating, the substances present in the mixture react with each other. For example, the tungsten reacts with the calcium fluoride so as to form tungsten fluoride and calcium. This reaction might be represented by the following equation:

$$W+3CaF_2 \rightleftarrows WF_6+3Ca$$

The produced volatile compound of the difficultly volatile metal and the readily volatile metal present in the mixture (in the present case, tungsten fluoride and calcium) evaporate off the electrode. In consequence thereof, the reaction, which is reversible, will take place as indicated by the equation. The evaporated substances are deposited on the wall of the tube and react again with each other owing to which the starting materials may be formed again. The reaction taking place in this case might be represented by the following equation:

$$WF_6+3Ca \rightarrow W+3CaF_2$$

Owing to this process, the conducting particles (the tungsten particles) and the chemical compound (in the present case the calcium fluoride) are present in the intermediate layer in a very finely divided and thoroughly mixed state, which is very favorable for the functioning of the photoelectric tube. Other difficultly volatile metals which may be successfully utilized are, for example, iron and zirconium, while the compound of the easily volatile metal which is heated together with the difficultly volatile metal may also consist, for example, of sodium chloride or potassium chloride.

In many cases it may be advantageous to add to the mixture heated in the tube another substance which facilitates the reaction or which produces partly other products. Thus, for example, silica may be added to the mixture containing tungsten and calcium fluoride. The reactions in this case might have the following course:

$$2W+6CaF_2+3SiO_2 \rightarrow 2WO_3+3SiF_4+6Ca.$$

During the heating of the mixture, the tube is connected to the vacuum pump whereby the very volatile silico-fluoride is removed from the tube.

The tungsten oxide and the calcium evaporate and settle on the wall of the tube. These substances react with each other which might be represented by the following equation:

$$WO_3+3Ca \rightarrow W+3CaO.$$

The intermediate layer thus produced consists of tungsten particles and calcium oxide.

Due to the addition of the silica to the mixture provided on the electrode 6, it is avoided inter alia that tungsten fluoride comes into contact with the glass of the wall which is thus prevented from being attacked by the said compound.

After the intermediate layer has been formed, the photo-active metal constituted, for example, by an alkali metal, may be introduced into the tube. This may be effected, for example, by evaporating the alkali metal from a lateral tube connected at 9 to the tube. A suitable method of introducing alkali metals into the tube is described, for example, in application for U. S. Letters Patent, Serial No. 360,993, filed May 6, 1929.

After the photo-active substance is applied to the intermediate layer, the tube may be closed and heated. If the photo-active substance is constituted by cesium, the tube may be heated, for example, to about 200° C. Due to the heating of the closed tube, the photo-active substance penetrates into the intermediate layer, thus giving rise to a decreased resistance of the photo-active electrode and to an increased emission of electrons. Not only the photo-active substance, which at the beginning of the heating operation is present on the intermediate layer, partly penetrates into the latter, but also the photo-active substance present in other points of the tube tries to penetrate into this layer due to the fact that during the heating of the tube it evaporates and deposits on the intermediate layer. Preferably, the quantity of the photo-active substance provided in the tube is such that after the closed tube has been heated all the photo-active substance present in the tube is present in the intermediate layer or is adsorbed by this layer so that in the tube the vapour pressure of the photo-active material is smaller than the normal pressure of the free material. Any superfluous photo-active material present in the tube may be removed therefrom by heating the tube while connected to the vacuum pump.

It is evident that the process in which a closed tube containing the photo-active material is heated to cause this material to penetrate into the intermediate layer can also be applied to a tube in which the photo-active substance is provided on an intermediate layer which does not yet contain conducting particles but which exclusively consists of a poorly conducting chemical compound. However, applicant has found that the penetration of the photo-active substance into the intermediate layer is facilitated if the latter already contains conducting particles.

It is also possible to apply the chemical compound present in the intermediate layer, and the photo-active substance, and, if desired, also other conducting particles, simultaneously to a substratum, owing to which the photo-active substance provided in the intermediate layer will be very intimately mixed with the chemical substance and with the conducting particles which might be present. In this case the photo-active substance constituted, for example, by cesium, may be developed in the tube or in the chamber connected thereto by heating a mixture of a compound of the photo-active metal, for example, cesium chromate, and a reducing agent, for

example, zirconium. If the mixture contains, in addition, a chemical compound which is volatile at the temperature to which the mixture is heated, the liberated photo-active metal and the said chemical compound precipitate simultaneously on the substratum.

To the mixture of the compound of the photo-active metal and the reducing agent may also be added a compound of a readily volatile metal, for example, sodium fluoride, which reacts with the reducing agent in the same manner as above described for tungsten and calcium fluoride. If the mixture consists, for example, of cesium chromate, zirconium and sodium fluoride, cesium will be liberated by some of the zirconium from the cesium chromate leaving oxides of chromium and zirconium and the remainder of the zirconium reacts with the sodium-fluoride to form zirconium-fluoride and sodium, which evaporate and, reacting in much the same manner as tungsten fluoride and calcium produce on the substratum again zirconium and sodium fluoride. The layer formed on the substratum consequently contains zirconium, sodium fluoride and cesium in a finely divided and thoroughly mixed state while at the surface of this layer a thin layer of cesium will be formed.

During the formation of the intermediate layer and the introduction of the photo-active substance into the tube, those parts of the wall of the tube on which precipitation is undesirable, may be maintained at a higher temperature than the other parts of the wall, so that a window 10 may be formed through which during the operation of the tube the rays of light are enabled to enter into the latter.

The window 10 may also be produced by screening with the aid of a shield a part of the wall of the tube during the formation of the intermediate layer and the introduction of the photo-active substance into the tube.

The tube, which is provided with an exhaust tube 11 allowing of connecting it to the pump, may be exhausted to the highest possible degree or may be filled with a gas, for example, a rare gas.

During the operation of the photo-electric tube represented, the electrode 6 is given a positive potential with relation to the photo-active electrode, which is subjected to radiation by light which can enter the tube through the window 10 and which causes the emission of electrons from the photo-active layer, the number of the electrons emitted depending upon the intensity of the light. It has been found that the photo-active electrode of the tube according to the invention may show a high emission of electrons while the electric resistance of this electrode is small.

Having now described our invention, what we claim and desire to secure by Letters Patent is the following:

1. A photoelectric cathode having a supporting surface, an intermediate layer comprising a chemical compound and electrically conducting particles on the supporting surface, and a photo-active substance coated upon said intermediate layer.

2. A photoelectric cathode comprising a supporting surface, an intermediate layer containing a chemical compound and conducting particles of a photo-active substance coated upon the supporting surface, and a photoelectric layer carried upon the intermediate layer.

3. A photoelectric cathode comprising a supporting base, a layer of photo-active substance, and an intermediate layer containing a chemical compound and photo-active electrically conducting particles.

4. A photoelectric cathode comprising a supporting base, a layer of photo-active substance, and an intermediate layer containing a chemical compound and metallic electrically conducting particles.

5. A photoelectric cathode comprising a supporting base, a layer of photo-active substance, and an intermediate layer containing a chemical compound and the combination of photo-active and metallic electrically conducting particles.

6. In the process of forming photoelectric tubes, the steps comprising depositing a layer of a mixture of electrically conducting particles and a salt upon a substratum, and applying photoelectric material upon the deposited layer.

7. In the process of forming photoelectric tubes, the steps comprising depositing by evaporation a layer of a mixture of electrically conducting particles and a salt upon a substratum, and applying photoelectric material upon the deposited layer.

8. In the process of forming photoelectric tubes, the steps comprising depositing a layer of a mixture of electrically conducting particles and a salt by double decomposition upon a substratum, and applying photoelectric material upon the deposited layer.

9. In the process of forming photoelectric tubes, the steps comprising depositing by evaporation and forming by double decomposition a layer of a mixture of electrically conducting particles and a salt, and applying photoelectric material upon the deposited layer.

10. In the process of forming a photoelectric tube, the steps which comprise heating a mixture of cesium chromate and zirconium containing also a volatile constituent capable of reacting with a reducing agent upon a base layer, and applying photoelectric material upon the deposited layer.

11. The process of preparing a photo-electric cathode which comprises, placing a mixture of a refractory metal and a compound of a readily volatile metal and an ultimately inactive element in an evacuated photo-envelope, heating said mixture to form a volatile compound of said refractory metal, exhausting said volatile compound formed from said envelope and, reacting the residual substances in vapor phase to reform one of the original materials and a different metal compound of another original metal compound as a finely divided and thoroughly mixed layer on the inner wall of said envelope, and finally vaporizing photo-electric material to be absorbed by said mixed layer.

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