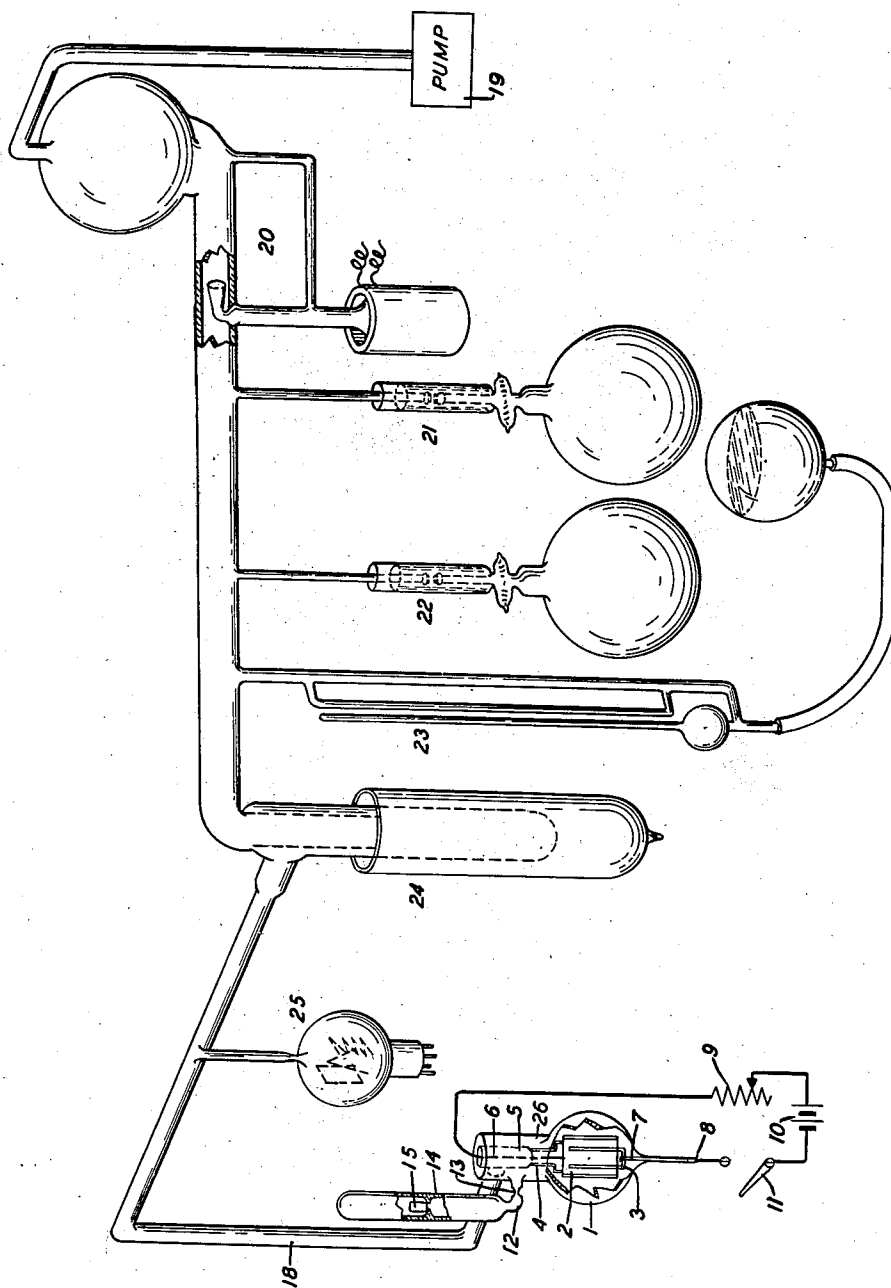


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PHOTOELECTRIC TUBE
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PHOTOELECTRIC TUBE

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This invention relates to photoelectric tubes and a method of making them.

In the manufacture of photoelectric tubes, it has been proposed to provide a light sensitive electrode comprising a self-supporting metal plate of conductive material, the surface of which is coated with a substance having characteristics different from the metal to produce a surface layer upon which a film of light sensitive material is deposited.

It has also been proposed to effect a result similar to that described above, by causing oxygen to chemically combine with the surface metal of the self-supporting plate and to deposit a film of light-sensitive material upon the resultant oxidized surface.

The present invention is directed to the production of an improved electrode of the type described in the preceding paragraph.

An object of the present invention is to condition a conductive member for use as an element of an electronically active electrode by causing a substance having characteristics different from the material of the member to combine with its surface and then reducing the combination.

Another object is to provide an electrode which is quantitatively conditioned to receive a film of electronically active material.

According to one illustrative embodiment of the invention for producing a light-sensitive electrode for use in a photoelectric tube, a polished plate of conductive metal, which is self-supporting, is enclosed in a container, heated to a high temperature in the presence of oxygen to produce a layer of oxide, the oxygen and impure gases are evacuated, and the member is then heated to a high temperature to reduce the oxide layer, whereby a roughened surface is produced. If the surface is not sufficiently rough, this cycle of operations may be repeated one or more times. After the roughening step is completed, oxygen is again introduced into the container and the plate is heated to oxidize the roughened surface to an extent determined by the amount of light-sensitive material to be deposited on it and the predetermined amount of light-sensitive material is then deposited upon the quantitatively conditioned surface. The conductive member may be heated in any suitable manner but preferably by ionic bombardment.

A detailed description of the embodiment of the invention, referred to above, follows and is illustrated in the attached drawing.

The single figure shows a schematic layout of

apparatus which may be employed to produce photoelectric tubes including an electrode made in accordance with this invention.

Referring to the drawing, there is shown a photoelectric tube comprising a bulb 1 provided with a neck 26, the bulb enclosing a plate 2 of conductive metal, the surface of which is treated in a manner to be hereinafter described to render it sensitive to light, and a fork-shaped anode 3. Plate 2 is mounted on supports 4 carried by a stem 5 and is connected to a lead-in conductor 6 passing through the stem, and anode 3 is carried by a support 7 and is connected to a lead-in conductor 8. The anode and plate 2 lie in parallel planes, are spaced apart a suitable distance and are supported so that they do not contact with the inner walls of the bulb.

The lead-in wires 6 and 7 are connected by an external circuit, including an adjustable resistance 9, a source of current 10 and a switch 11, which is used in a manner and for a purpose to be described below while the tube is being manufactured. Upon completion of the tube the wires 6 and 7 are employed to connect the electrodes to an operating circuit.

The bulb 1 is connected by a tube 12 having a restriction 13 to a side tube 14 enclosing a metal container 15, carrying a mixture adapted when heated, to react and give off a definite amount of caesium.

A tube 18 serves to connect the bulb with a pumping system, which comprises a vacuum pump 19, mercury vapor pump 20, an apparatus 21 for introducing an inert gas into the bulb, an apparatus 22 for introducing oxygen into the bulb, a McLeod pressure gauge 23, a liquid air trap 24 and an ionization gauge 25.

The method of manufacturing photoelectric tubes, using the equipment illustrated, will now be described.

The bulb 1 is heated either in a furnace or by a hot flame to liberate occluded gases and the metallic elements within the bulb are heated by a high frequency induction furnace to drive off absorbed gases. At the same time, the pumping system, is operated to evacuate the liberated gases.

The pumping system is continued in operation until the desired degree of vacuum is attained within the bulb. The pump is then shut off and heating of the bulb and electrodes is discontinued.

The assembly is now purged by admitting oxygen from the apparatus 22 into the bulb and pumping it out, after which the polished surface of the plate 2 is conditioned by admitting a fresh

charge of oxygen into the bulb from the apparatus 22 and intermittently operating the switch 11 to cause to occur between the electrodes a series of heavy current discharges separated by intervals when no current discharge takes place. The succession of discharges is thereby controlled to occur for definite periods of time, separated by other periods of no discharge. The length of the respective periods is so regulated that the plate is ionically bombarded, whereby it is heated to a high temperature and allowed to cool to a low temperature. The electric discharges cause ionization of the oxygen and results in the surface of the plate acquiring a heavy layer of oxide. This layer is then decomposed or reduced by ionic bombardment, either intermittent or continuous, whereby the plate is restored to its natural color but its surface is roughened to an extent which can be seen by the naked eye.

Conditioning of the surface of the plate, as described above, may be accomplished by using oxygen at a pressure of 3 or 4 mm. of mercury and supplying current at 600 volts through a 200 ohm resistance to the lead-in conductors 6 and 8. If the surface of the plate is not sufficiently roughened, this conditioning cycle may be repeated one or more times.

The bulb is then evacuated, and the plate is allowed to cool. A fresh charge of oxygen is introduced into the bulb, and the plate is again bombarded with several quick flashes, separated by time intervals sufficiently long to allow the plate to cool. The amount of oxide on the plate may be determined approximately by controlling the pressure of the oxygen, the impressed voltage and the length of the intervals of time during which current is discharged between the electrodes, and these conditions should be so regulated that a thin oxide coating is produced upon the roughened surface of the plate. During this oxidizing period, care should be exercised to make the time during which the flashes occur so short that the plate is not heated to a temperature which would cause the oxide layer to be reduced. This operation should be continued until there is produced on the roughened surface a layer of oxide just sufficient to combine with a predetermined amount of caesium, i. e. adequate to produce a light reactive film of the desired sensitivity. If this layer is too thin there will be an excess of caesium and the caesium-oxygen compound produced will be unstable. If the oxide layer is too thick a more stable compound will be produced, but its sensitivity to light when given the usual final heat treatment will not be great.

The pressure of oxygen used in producing the thin oxide coating is slightly lower than that used in the roughening stage, approximately 2 mm. of mercury has proven satisfactory.

The desired degree of oxidation of plate 2 having been effected, the pumping system is started to evacuate the free oxygen remaining in the bulb 1. After a desired degree of vacuum has been attained, the metal container or capsule 15 containing the chemical mixture is heated to cause the mixture to react and liberate a fixed amount of alkali metal, i. e. sufficient to cause the desired reaction with the conditioned surface of the plate.

In the embodiment herein described the plate 2 is silver and the material enclosed in the capsule consists of barium azide BaN_6 and caesium chloride CsCl . The metallic container is heated by induced high frequency current to from 100° to 150°C. , whereby the barium azide is reduced to

give off nitrogen and leave metallic barium. The container is then heated to about 400°C. , whereby the barium reduces the caesium chloride completely and pure caesium is liberated and deposits on the walls of the tube 14. By controlling the quantity of the $\text{BaN}_6\text{-CsCl}$ mixture, the amount of caesium produced may be fairly accurately determined. The tube 14 is now heated while the bulb and its neck are cooled, this causes the caesium to distill into and deposit upon the walls of the neck 26 and the stem 5. After this has been effected the walls of the bulb per se are maintained cool and heat is applied to the neck 26, whereby the caesium deposited upon the neck and stem 5, is vaporized and caused to deposit upon the walls of the bulb 1.

A small heating furnace, which has been previously heated to 100° or 150°C. , is raised around the whole photoelectric tube. This causes the caesium to leave the glass walls and deposit on the silver cathode plate 2. By having the electrodes 2 and 3 enter opposite ends of the tube, leakage across the glass is small and the photoelectric activity of the cathode may be carefully watched during heat treatment of the tube, without causing large leakage or dark currents to flow between the electrodes.

The furnace used is designed to have a small window through which light may be focused on the cathode whereby its photoelectric activity may be watched during the heat treatment.

The maximum temperature used at this stage is approximately 240°C. , and the time required to cause combination of the silver oxide and caesium metal varies with the relative amounts of oxygen on the silver and caesium let into the tube. When the caesium first strikes the oxidized silver plate the color of the plate changes and may assume a grayish green or charcoal black appearance. The photoelectric activity in this condition may not be very great, but it is generally of the same order of sensitivity as a standard potassium hydride photoelectric tube. As the heat treatment is continued a thermionic current manifests itself with the photoelectric effect superimposed on it. The appearance of this thermionic current at a temperature of approximately 150°C. is evidence that the work function of the surface has been materially decreased. The heat treatment is continued until the combined currents due to the thermionic and photoelectric effects is at a maximum. This time may be any where from twenty minutes to one hour, depending upon the relative amounts of silver oxide and caesium metal let in the tube.

When the furnace is removed the thermionic current decreases and the photoelectric current increases.

When the tube evidences the desired sensitivity, inert gas, for example, argon, at the desired low pressure, is admitted into the bulb from the apparatus 21, pumping is discontinued, the tube is sealed off from the pumping apparatus and is ready for use.

The plate member 2 may consist of any good conductive material, and any photo-sensitive material may be used for the light sensitive film.

What is claimed is:

1. A method of preparing a cathode for a light sensitive device which comprises providing a metallic cathode member in an evacuated container, introducing into the container an element having characteristics different from the member, chemically combining a surface layer of said member with said element by ionic bombardment

of the surface of the member, further ionically bombarding said member to decompose the resulting combination, and providing a light sensitive electron emissive surface on the member.

2. A method of preparing a cathode for a light sensitive device which comprises providing a metallic cathode member in an evacuated container, introducing oxygen into the container, combining said oxygen with a surface layer of said member to produce a layer of oxide, reducing said oxide layer, and providing a light sensitive electron emissive surface on the member.

3. A method of preparing a cathode for a light sensitive device which comprises providing a metallic cathode member in an evacuated container, introducing oxygen into the container, ionically bombarding the member to produce oxidation of a surface layer of said member, reducing said oxide layer, and providing a light sensitive electron emissive surface on the member.

4. A method of preparing a cathode for a light sensitive device which comprises providing a metallic cathode member in an evacuated container, introducing oxygen into the container, ionically bombarding the member to produce oxidation of a surface layer of said member, decomposing said oxide layer by heating, and providing a light sensitive electron emissive surface on the member.

5. A method of preparing a cathode for a light sensitive device which comprises providing a metallic cathode member in an evacuated container, introducing oxygen into the container, ionically bombarding the member to produce oxidation of a surface layer of said member, decomposing said oxide layer by ionic bombardment, and providing a light sensitive electron emissive surface on the member.

6. A method of producing a cathode comprising a member coated with electron emitting material which comprises oxidizing the surface of the member, reducing the oxide coating, again oxidizing the surface of the member, and vaporizing an electron emitting material which is deposited on the oxidized surface.

7. A method of producing a light sensitive de-

vice comprising a bulb enclosing an anode and a cathode member which comprises oxidizing the surface of the member, reducing the oxide coating, again oxidizing the surface of said member, vaporizing a light sensitive material, causing said vaporized material to deposit on the bulb, and heating the bulb to cause the light sensitive material to be transferred to the oxidized surface of said member.

8. A method of producing a cathode for a photoelectric tube which consists of forming a silver oxide coating on a cathode plate, heating the plate to reduce the silver oxide, cooling the plate, reoxidizing the plate, and forming a light sensitive electron emissive surface on the plate.

9. The method of producing a light responsive electron emissive surface which comprises the following steps, roughening a metallic surface, oxidizing said surface and depositing an alkali metal thereon.

10. A method of providing a light sensitive surface on the cathode of a photoelectric tube which comprises mounting a metallic cathode in an envelope, exhausting the envelope, outgassing the cathode and envelope by heating, admitting oxygen to the envelope, combining the oxygen with the surface metal of the cathode to oxidize the cathode surface, converting this oxidized surface to the metallic state by heating, again oxidizing this surface, and coating the oxidized surface with a light sensitive film of alkali metal.

11. A method of producing a light sensitive tube comprising a bulb enclosing an anode and a conductive member which comprises connecting to said bulb a receptacle containing a mixture adapted to react to produce light sensitive material, evacuating said bulb and receptacle, providing a metallic oxide coating on said member, reducing the oxide coating, oxidizing the surface of the member, heating said mixture to a reaction temperature to produce light sensitive material in vapor form, and heating said receptacle and bulb to drive said vapor to the oxidized surface of said member.

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