June 11, 1946. R. B. JANES 2,401,737

PHOTOTUBE AND METHOD OF MANUFACTURE

Filed March 14, 1942

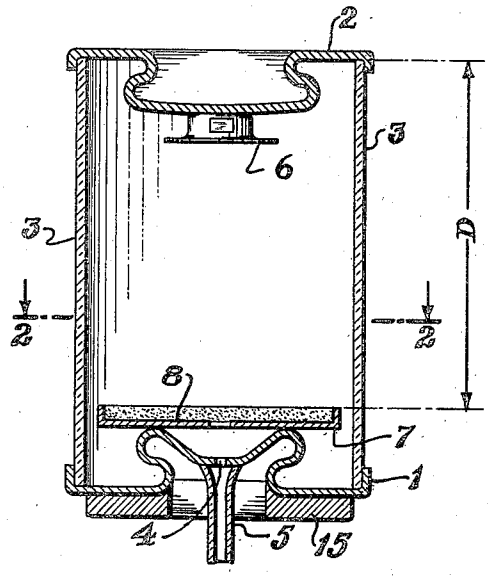

FIG. 1

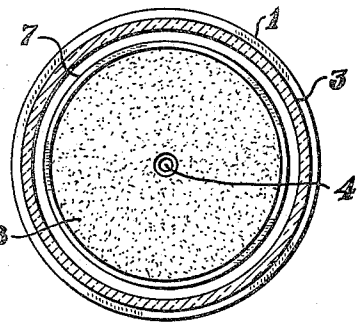

FIG. 2

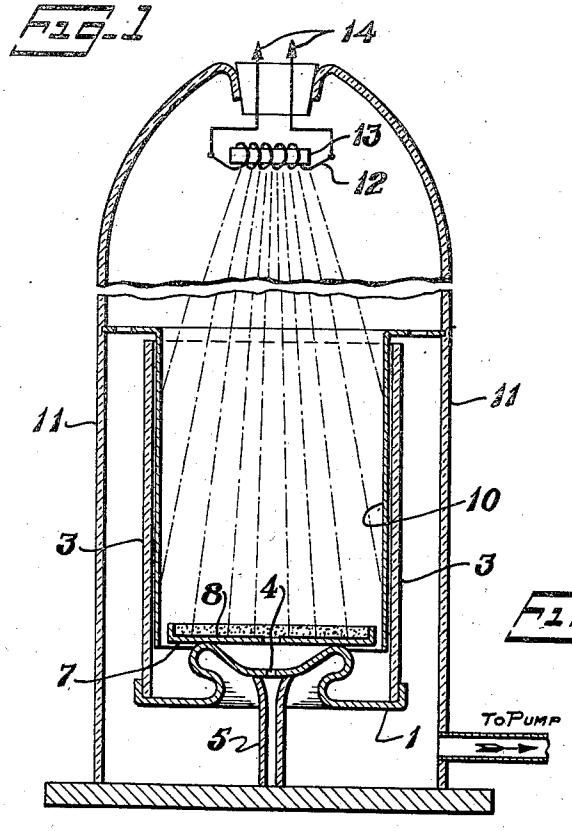

FIG. 3

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PHOTOTUBE AND METHOD OF MANUFACTURE

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12 Claims. (Cl. 250—165)

1

My invention relates to photoelectric tubes and their method of manufacture and particularly to tubes incorporating coatings of elements, such as antimony, arsenic or bismuth sensitized with an alkali metal.

This application is an improvement over my copending original application, Serial No. 342,199, filed June 25, 1940. In my said application I disclosed methods for manufacturing phototubes having alkali metal sensitized cathodes formed by a step of evaporating and condensing a quantity of antimony, arsenic or bismuth on a cathode foundation. While the phototubes therein described offer great advantages over tubes of the prior art, the mechanical construction renders the tubes somewhat fragile and subject to structural failure in certain applications where great ruggedness is necessary. From a time prior to filing of my said original application, I have made many phototubes in attempts to obtain a more rugged structure suitable for use in applications wherein the tubes are subjected to high values of acceleration both longitudinally of the tube and when the tube is subjected to circumferential acceleration, such as a whirling motion. Thus, certain applications require a high degree of ruggedness to withstand such accelerations which are several thousands times the force of gravity. While various structural modifications are possible with conventional phototubes utilizing an alkali metal sensitized oxygen treated silver cathode, such features are difficult to incorporate in tubes of the antimony, arsenic and bismuth types because of the instability of the antimony cathode during tube assembly and processing. Furthermore, I have found that any oxidation of such a cathode during processing, such as while sealing the cathode within an envelope, is exceedingly detrimental to the cathode.

It is an object of my invention to provide a rugged phototube of the antimony coated cathode type. It is a further object to provide a phototube of the type described which will withstand high forces of acceleration without distortion or mechanical failure of the parts or variation in the operating characteristics of the tube. It is a further object to provide an improved method of manufacturing a rugged phototube of the antimony, arsenic and bismuth cathode type; and it is still a further object to provide a method of manufacture wherein deleterious effects upon an antimony coated cathode may be minimized or entirely eliminated. In accordance with my invention I provide a phototube having two end closure caps preferably of metal sealed to opposite

2

ends of a tubular insulating member preferably of glass wherein one of the caps supports an antimony, arsenic or bismuth coated cathode foundation facing the opposite cap or is itself the foundation for such a coating, the other or opposite cap supporting a source of alkali metal for activating the cathode coating. Further in accordance with my invention I provide a method of manufacturing a phototube of the above type wherein one closure cap is sealed to the tubular member prior to the formation of the condensed coating on the cathode foundation while protecting the tubular member from condensation of the coating material, such as antimony, followed by sealing of the other closure cap to the member without damaging the coating and the photoactivation of the coating. These and other objects, features and advantages of my invention will become apparent when taken with the following description and the accompanying drawing wherein—

Figure 1 is a view in longitudinal section of a rugged phototube made in accordance with my invention;

Figure 2 is a cross section of the tube of Figure 1 taken along the lines 2—2; and

Figure 3 shows an apparatus suitable for performing one of the principal operations in the manufacture of my phototube.

In the following description I will refer specifically to antimony coatings and, it will be appreciated that either arsenic or bismuth may be substituted for the antimony without departing from the scope of my invention.

In accordance with my invention I have found that a tube of the type described in my said original application is subject to injury of the photocathode during tube manufacture of it any time during the formation of the antimony coating, this coating should become overheated, especially when such overheating occurs in the presence of a normal oxygen-containing atmosphere. Thus, while tubes of this type offer many advantages over those of the prior art, particularly in ease of manufacture wherein a cathode foundation is provided with an antimony, arsenic or bismuth coating in a rarified atmosphere, subjected to the normal atmosphere and then sealed within an envelope; such a procedure when applied directly to the manufacture of an exceedingly rugged tube produced poor photosensitivity. I have found that a minimum distance must be maintained between the cathode foundation and the envelope seal when following my prior teaching of sealing an antimony, arsenic or bismuth coated cathode

in an envelope and that while the construction shown in my said application is satisfactory for the relatively large tubes shown therein, additional precautions must be followed and the sealing steps performed in a definite sequence to provide a rugged tube of the type shown in Figure 1. Referring to Figure 1 wherein I show a phototube made in accordance with my invention, the tube comprises principally two end closure caps 1 and 2 sealed to opposite ends of a tubular insulator, such as a short length of glass tubing 3. Preferably one of the closure caps is apertured as shown at 4 and is provided with a glass tubulation 5 sealed around the aperture. The opposite closure cap 2 is non-apertured and supports a source 6 of alkali metal, such as a caesium compound reducible by heating to caesium. As indicated above the closure cap 1 may serve as a foundation for the cathode coating although I prefer to attach a metal disk 7 to the cap 1 as shown. Further in accordance with my invention, I provide a coating 8 on the foundation 7 or on the inner surface of the closure cap 1 of antimony, arsenic or bismuth which is at a predetermined minimum distance D from the seal between the opposite end cap 2 and the tubing 3.

More particularly and in accordance with my invention I have found that it is not only desirable but necessary to provide the coating 8 of antimony either on a foundation, such as the metal disk 7, or directly on the inner surface of the cap 1 at a definite time during the manufacturing steps to prevent injury to this coating during subsequent steps of the manufacturing process. For example, if the coating 8 is subjected to relatively high temperature, such as occurs when the closure cap 1 is sealed to the glass tubing 3, permanent injury of the coating 8 occurs. Thus, as pointed out in my said copending application, the antimony cathode coating should not be oxidized and I believe that my sequence of processing steps avoids or substantially eliminates material oxidation of the antimony coating on the foundation. Furthermore, the closure cap 1 must be subjected to certain processing to provide good sealing properties at the time the seal is made to the glass tubing 3. Therefore, in accordance with my invention I so treat the closure cap prior to the application of the coating 8 such that a good seal may be made followed immediately by making the seal prior to the application of the coating 8, and further in accordance with my invention I deposit the coating 8 of antimony by evaporation and condensation steps without providing a coating of antimony on the glass tubing 3.

The closure caps 1 and 2 are preferably of material such as chrome-iron having a coefficient of expansion substantially matched with that of the glass of the tubing 3. A chrome-iron which I have found satisfactory for use with lime glass contains as its principal constituents—

	Per cent
Chromium	26–30
Nickel	0.5
Silicon	0.5
Manganese	0.5
Iron	Balance

Following formation of the closure cap metal to a satisfactory form one cap for each tube is apertured as shown at 4 in the drawing, and where the use of a foundation member other than the cap is desired, the disk 7 is attached to the cap 1, such as by welding. The material of the disk 7 is preferably nickel although a similar chrome-iron may be used and the welding operation should be done with a minimum of heating to avoid puncture of the metal of the cap 1, inasmuch as the cap forms a closure for the completed phototube following the welding of the disk 7 to the cap 1. I then oxidize the cap by heating it in moist hydrogen to provide a coating of oxide which is conducive to the manufacture of a good seal to the glass of the tubing 3. Such oxidation by heating in moist hydrogen is well known in the art and is described by Hull, Burger and Navis in an article entitled, "Glass-to-metal seals," part 2, Journal of Applied Physics, volume 12, No. 9, September 1941, pages 698 to 707. For the metal composition given above heating of the caps in moist hydrogen for 6 minutes at a temperature of 1150° C. is sufficient to provide a suitable oxide coating which appears to be chromium oxide. Following the oxidation step I prefer to seal the tubulation 5 to the oxidized cap 1 around the aperture 4 so that following complete assembly, the tube may be evacuated and further processed in accordance with my prior teaching. Preferably the tubulation 5 is of lead glass which has the property of absorbing excess alkali metal during tube processing. Simultaneously or sequentially with the sealing of the tubulation 5, I seal the periphery of the cap 1 to the glass of the tubing 3 to provide an hermetic seal and prevent leakage of air within the tube during and following evacuation. Following the sealing steps I clean the inner surface of the cap 1, if it is to be used as the cathode foundation, or clean the upper surface of the disk 7 to provide a clean surface on which to form the antimony 8. This cleaning operation may be performed by buffing or by electrolytic cleaning wherein the cap 1 is made the anode in an electrolytic bath, a portion of the metal thereof or of the disk 7 being deplated to provide a clean surface. The disk 7 or inner surface of the cap 1 is then ready to receive a coating of antimony which I apply in accordance with my invention in apparatus such as shown in Figure 3. Referring to Figure 3 I insert the glass tubing 3 over a tubular or cylindrical open-ended shield 10, the shield extending to within close proximity or slightly overlapping the foundation, such as the disk 7 or the inner surface of the cap 1, on which the antimony is to be deposited. The shield 10 is preferably supported within a chamber or bell jar 11 capable of being evacuated. I also support opposite the disk 7 and the cap 1 a source of antimony to be vaporized and condensed upon the cathode foundation. Such a source of antimony may comprise a refractory metal coil 12 supporting a quantity of antimony 13 or other metal such as arsenic or bismuth which may be vaporized by passing an electric current from a battery or other current source through the connecting leads 14. Following the insertion of the glass tubing 3 over the shield 10 I evacuate the bell jar 11 to a high vacuum, the residual air pressure preferably being less than 0.5 micron, and I then evaporate a sufficient quantity of antimony from the source 13 to provide the coating 8 of the desired thickness. I have found that a thickness corresponding to 0.1 to 0.16 milligram per square centimeter is sufficient to provide good photosensitivity when such a coating is treated with alkali metal. The rate of condensation of antimony to form the coating 8 is preferably less than 0.2 milligram per square centimeter per minute, since I have found that

a higher rate of condensation may be detrimental and form a non-uniform coating. The entire bell jar assembly with the exception of the coil 12 and the heated antimony source 13 is preferably maintained at room temperature during the evaporation and condensation steps, except for such slight heating of the disk 7 which may occur by the radiation from the coil 12. Obviously while I have shown a form of bell jar 11 suitable for coating only one foundation at a time, a plurality of shields, such as the shield 10, may be located around a centrally disposed source of antimony so that a number of cathodes may be processed simultaneously. Following the formation of the antimony coating 8, I remove the glass tubing 3 from the shield 10 and close the open end of the glass tubing 3, with the cap 2 to which is attached a source of alkali metal 6 which may be subsequently vaporized and condensed on the antimony coating 8. Obviously the cap 2 may be oxidized in a manner similar to that of the cap 1 prior to the sealing operation and preferably prior to the attachment of the alkali metal source 6 thereto. I have found that in tubes made in accordance with my invention, the sealing of the cap 2 to the glass tubing 3 does not have any detrimental effects upon the antimony coating 8 provided the distance D, in Figure 1, is at least ¾ inches and the cathode foundation is cooled during the sealing operation. In accordance with this teaching of my invention I maintain heat conductive means in contact with the closure cap 1 during the time the opposite cap 2 is sealed to the glass tubing 3. Referring again to Figure 1 I have shown a relatively large metal member 15 which is maintained in metallic contact with the cathode foundation during the sealing step. The mass of the member 15 may be sufficient to absorb the heat from the cap 1 or disk 7 although the member 15 may be artificially cooled. The temperature of the cathode should be not higher and preferably less than 150° C. during this sealing operation, higher temperature being detrimental. Satisfactory cooling is shown by the absence of any color change of the coating 8, excessive temperatures resulting in a color change to a light yellow or red. It should be noted that the construction of my tube shown in Figure 1 is particularly adapted to this method of cathode cooling. In addition the member 15 may be used to push the glass tubing 3 into contact with the cap 2 during the sealing operation thereby working the glass slightly and causing it to seal to the chrome-iron to better advantage.

It will be noted that in accordance with my teaching contained in my original application, the foundation bearing the antimony coating 8 is removed from the bell jar and is subjected to normal atmospheric conditions. I have found that the relative humidity of the atmosphere to which the coated cathodes are subjected should be low and preferably less than 80 per cent relative humidity at 25° C. which corresponds to a water vapor concentration in the atmosphere equivalent to 8 grains of water vapor per cubic foot of air. The satisfactory results obtained are believed to be due to the fact that antimony does not oxidize when subjected to normal atmospheric conditions at room temperature as I have been unable to find any trace of antimony oxide on the antimony coating following such treatment. However, cathodes subjected to normal atmospheric conditions appear to give better results than cathodes not so treated.

In accordance with my original application I do not oxidize the antimony coating during the tube processing so that following the sealing of the cap 2 to the glass tube, I immediately exhaust the tube through the tubulation 5 and bake at a temperature of 275 to 310° C. to remove any occluded gases within the tube. Following the baking which may be from 15 minutes to ½ hour, I vaporize a quantity of alkali metal, such as caesium, from the source 6. I have found that the temperature of the antimony coating 8 during this caesium vaporization is not critical and may vary from room temperature up to the baking temperature of the tube. Following the vaporization of the alkali metal, the tube is baked preferably at a temperature of 160° C. for 30 minutes and during this baking I believe that the alkali metal combines with the antimony coating 8 to provide a photocathode having a very high sensitivity to light. Following the baking the tubulation may be tipped off, and the tube removed from the pump and aged in a manner described in my said original application to stabilize the photoelectric emission from the cathode.

In operation the cap 1 serves as a cathode connection and is operated at a negative potential with respect to the cap 2 serving as the anode. Electrons liberated from the coating 8 in electrical contact with the cap 1 are drawn to the anode cap 2, the electrons being substantially proportional to the light incident upon the coating. The disclosed structure is ideally adapted to multi-directional use since the cathode coating is exposed from all sides facing the anode. Furthermore, inasmuch as the cathode coating faces the anode directly, is symmetrical therewith, and at a uniform distance therefrom, the effects of wall charges described in detail in my copending application, Serial No. 425,730, filed January 6, 1942, are minimized so that electron collection does not vary substantially with variation in anode potential.

While I have described my invention with particular reference to a phototube having a glass envelope closed at opposite ends with a metal cap and the preferred method of manufacturing such a tube, it will be appreciated that various modifications may be made both in the structure and the method of manufacture without departing from the spirit of my invention or the scope thereof as set forth in the appended claims.

I claim:

1. A phototube comprising a tubular glass envelope, a metal closure at each end of and forming the end walls of said envelope, a coating of an element which when sensitized with alkali metal is photosensitive facing and removed from one of said closures and directly adjacent the other of said closures, and a source of alkali metal supported by said one closure to sensitize said coating.

2. A phototube comprising a tubular glass envelope, a metal cap sealed to each end of said envelope, a coating of an element which when sensitized with an alkali metal is photosensitive supported by one of said metal caps in a position directly facing and exposed to the other of said caps and an alkali metal deposited on said coating.

3 A phototube comprising a tubular envelope of transparent insulating material, an individual metal cap sealed to and closing each of the opposite ends of said envelope, a coating of an element selected from the group consist-

ing of the elements antimony, arsenic, and bismuth on one of said caps and a quantity of alkali metal deposited on said coating to render said coating electron emissive.

4. A phototube comprising a cylindrical glass envelope of predetermined length, a metal closure cap hermetically sealed to each end of said envelope, a coating of an element selected from the group consisting of the elements antimony, arsenic and bismuth adjacent one of said caps, substantially the entire surface of said coating facing the opposite cap and removed therefrom by a distance of at least three quarters of an inch whereby the sealing of said opposite cap does not injure said coating, and an alkali metal deposited on said coating to render the coating photoemissive.

5. A phototube comprising a cylindrical glass envelope, a metal cap at each end of said envelope, one of said caps being apertured and closed by an exhaust tubulation, a cathode foundation affixed directly to one of said caps and directly exposed to and facing the other of said caps, and a coating of alkali metal treated antimony on the exposed side of said foundation.

6. A phototube comprising a tubular glass envelope of predetermined length, a metal cathode support cap sealed directly to and closing one end of said envelope, an anode cap sealed directly to and closing the other end of said envelope at a distance of at least three quarters of an inch from the junction between said cathode cap and said envelope, said caps extending transversely of said envelope, a coating of antimony substantially coextensively with the surface of said cathode cap facing said anode cap, and a quantity of alkali metal deposited on said antimony coating.

7. The method of manufacturing a phototube having two closure caps separated by a tubular insulating member comprising sealing one of said caps to one end of said member, depositing an element selected from the group consisting of the elements antimony, arsenic and bismuth on a surface in electrical contact with and substantially coextensive with the cap sealed to the said one end of said member, then sealing the other cap to the other end of said member without heating the deposited element to a temperature at which it becomes oxidized, exhausting the envelope formed by said member and said closure caps, baking said envelope and sensitizing said deposited element with an alkali metal.

8. The method claimed in claim 7 including the step of maintaining the deposited element at a temperature not greater than 150° C. during the sealing of said other cap to said member.

9. The method of manufacturing a phototube having an envelope of two closure caps sealed to and separated by a section of glass tubing comprising the steps of sealing a metal cap to one end of said tubing, depositing antimony on a surface closely adjacent and in metallic contact with said sealed metal cap, sealing another cap on the opposite end of said tubing by heating said tubing and said other cap to facilitate sealing, simultaneously cooling said metal cap by conduction to a metallic member exterior to said envelope to maintain said deposited antimony at a temperature less than 150° C. during said second-mentioned sealing step, evacuating and baking said envelope, and sensitizing said deposited antimony with an alkali metal.

10. The method of manufacturing a phototube having a tubular glass envelope closed at opposite ends by metal closure caps comprising the sequential steps of welding a cathode foundation to a metal cap, oxidizing said cap, sealing said cap to one end of said glass envelope, cleaning said foundation of any oxide thereon, depositing antimony on said foundation while protecting the inner wall of said envelope against deposition of antimony thereon, sealing a cap to the opposite end of said envelope while maintaining said foundation at a temperature less than 150° C., exhausting and baking said envelope and sensitizing the deposited antimony with an alkali metal.

11. The method of manufacturing a phototube having two closure caps separated by a tubular insulating member comprising sealing one of said closure caps to one end of said tubular member, inserting an open-ended shield within the open end of said member to within close proximity of the closure cap sealed to said member, evaporating a material which when sensitized with an alkali metal is photosensitive, condensing said material on a surface adjacent said closure cap while the inner walls of said tubular member are protected by said shield, removing said shield, sealing the other closure cap to the open end of said insulating member and photosensitizing the condensed material with an alkali metal.

12. The method of manufacturing a phototube having two metal closure caps on opposite ends of an insulating envelope comprising fastening a cathode foundation to one closure cap, sealing said cap to one end of the envelope, inserting a shield member within the open end of said envelope of sufficient length to extend at least to said cathode foundation, evaporating and and condensing antimony on said foundation in the presence of a non-oxidizing atmosphere, subjecting said condensed antimony to normal atmospheric conditions, removing said shield member, sealing the other closure cap to the open end of said envelope, exhausting said envelope, and sensitizing said condensed material with an alkali metal.

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