Nov. 25, 1947. R. B. JANES 2,431,402

PHOTOTUBE AND METHOD OF MANUFACTURE

Filed March 31, 1943

Fig. 1.

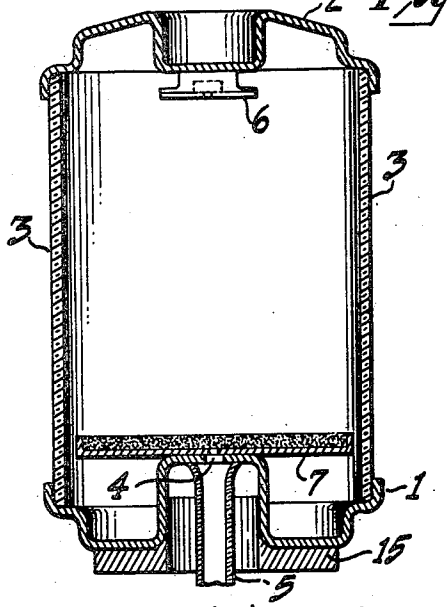


Fig. 2.

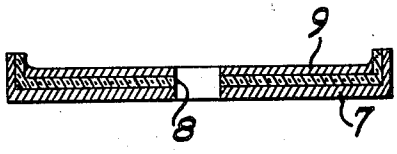


Fig. 4.

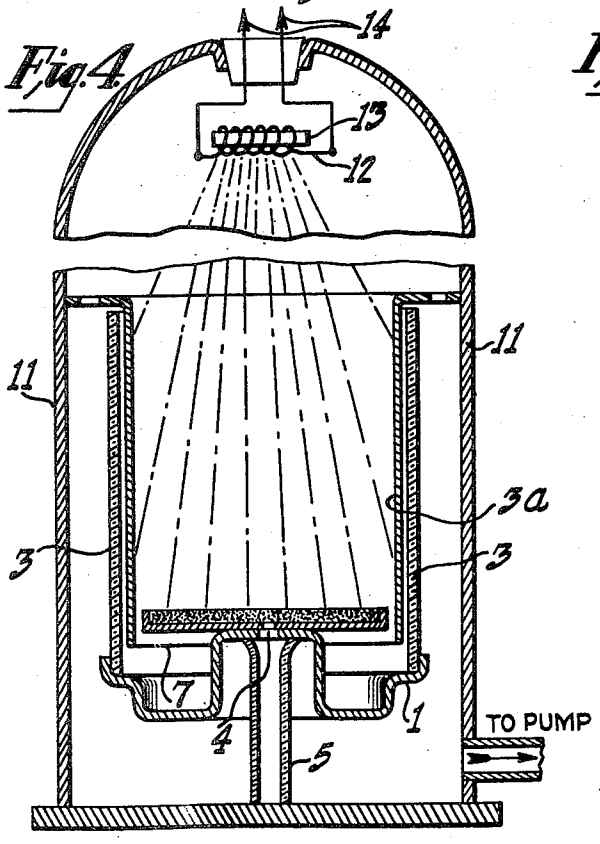
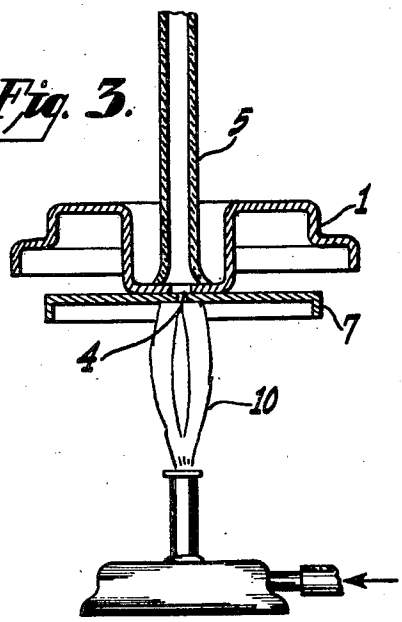


Fig. 3.



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PHOTOTUBE AND METHOD OF MANUFACTURE

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14 Claims. (Cl. 250—165)

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

This application is a continuation-in-part of my copending application, Serial No. 434,681, filed March 14, 1942. In my said application I disclosed a phototube having oppositely disposed metal closure caps, the envelope being completed therebetween by a short length of glass tubing serving as an insulator between the closure caps. One of the closure caps supported an antimony, arsenic or bismuth coating either on the inner surface of the cap or on a cathode foundation and directly faced the opposite closure cap which supported the alkali metal source for activating the coating on the cathode foundation. Such a structure is very rugged and is 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 angular acceleration such as a whirling motion about its longitudinal axis. Such a tube structure is thus able to withstand high accelerations which may be several thousand times the force of gravity. Phototubes having an alkali metal treated antimony, arsenic or bismuth coating are highly sensitive to light rich in the blue portion of the spectrum and from a date prior to my original application the need for higher sensitivities to light in this portion of the spectrum has been recognized. In addition, while my original application disclosed and claimed methods of manufacture wherein this type of tube was capable of large production manufacture, some loss or shrinkage occurred rendering the processing of these tubes quite critical. For example, slight changes in temperature and in handling of the parts so varied the manufacturing conditions that the percentage of good tubes during manufacture was not as high as desired.

It is an object of my invention to provide a photoemissive electrode and phototube of the antimony coated type which may be manufactured with wide ranges of manufacturing tolerances. It is another object to provide a phototube of the type described which is easier to manufacture than prior tubes and which has exceptionally high photosensitivity especially to light

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in the blue portion of the spectrum. It is a further object to provide an improved method of manufacturing a phototube of the antimony, arsenic or bismuth coated cathode type. In accordance with my invention I provide a phototube envelope such as of the type having two metal end closure caps sealed to opposite ends of a tubular insulating member preferably of glass and I provide within the envelope a thin coating of antimony, arsenic or bismuth on a thin oxide film formed integrally with an oxidizable metal such as one of the caps, the opposite cap preferably supporting a source of alkali metal for activating the cathode coating. Further, in accordance with my invention, I provide a cathode foundation of an oxidizable metal such as chromium or a metal foundation including a high proportion of chromium as an alloy constituent so that a highly heat insulating film may be provided integrally with the foundation to form a support for the antimony, arsenic or bismuth coating. Still further, in accordance with my invention, I provide a method of manufacturing a phototube wherein a cathode foundation containing chromium is oxidized to form a thin film of chromic oxide on which the antimony or similar metal is deposited, heat treated under predetermined conditions and sensitized with an alkali metal. These and other objects, features and advantages of my invention will become apparent when taken in connection with the following description and accompanying drawing wherein:

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

Figure 2 is a cross-sectional view of an electrode shown in the phototube of Figure 1.

Figure 3 is a view showing a preferred method of one of the manufacturing steps in practicing my method of manufacture; and

Figure 4 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 as a cathode coating and it will be appreciated that either arsenic or bismuth may be substituted in whole or in part 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 if at 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 containing water vapor. Consequently, in accordance with my invention, I provide a structure and method of manufacture wherein the temperature of the antimony coating may be reduced especially during the manufacturing steps when the coated foundation is inherently subjected to an oxygen and water vapor containing atmosphere. Therefore, in accordance with my invention, I provide a cathode foundation of a specific metal or alloy which is preferably a poor heat conductor and which contains a metal which may be oxidized to form an insulating support for the subsequently applied antimony coating.

Referring to Figure 1 wherein I have shown a phototube made in accordance with my invention, the tube comprises 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 nonapertured and supports a source 6 of alkali metal such as a caesium compound reducible by heating to caesium. I may provide the closure cap 1 of a metal which is suitable, when oxidized, as a foundation for the antimony coating, although I prefer to provide a metal disc 7 attached to the cap 1 which serves as the cathode foundation and as a massive support for the antimony coating with an intermediate film of insulating material formed integrally with the cathode foundation.

Referring to Figure 2, I have shown the metal disc 7 which is of chromium or an alloy thereof such as a nickel chrome alloy, the chromium exposed at the surface thereof being oxidized to form a thin film 8 of chromic oxide prior to the deposition of the thin film of antimony 9.

While the disc 7 may be oxidized prior to its attachment to the cap 1, I prefer to first weld the disc to the cap as shown in Figure 1, the cap being of a metal which will seal easily to the glass tubing 3. For this purpose I prefer to use a cap of chrome iron, the principal constituents of which may be:

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

Following welding of the cap 1 and metal disc 7, the assembly thus formed may be oxidized by firing in moist hydrogen such as described by Hull, Burger and Navis in an article entitled "Glass-to-metal seals," part 2, Journal of Applied Physics, vol. 12, No. 9, September, 1941, pp. 698–707. Such firing produces a relatively thick coating or film of greenish colored chromic oxide integral with both the chromium containing disc 7 and the chrome iron cap 1, so that the cap may be hermetically sealed to the glass tubing 3, the firing likewise producing a suitable coating of greenish chromic oxide 8 as shown in Figure 2 on the disc 7 to serve as a foundation for the coating of antimony 9. I have found that during the firing in moist hydrogen some hydrogen is adsorbed

both in the cap 1 and in the disc 7 which may diffuse into the tube following exhaust. Thus when such hydrogen firing is used, I prefer to bake the assembly or assemblies in a nonoxidizing atmosphere such as nitrogen or a vacuum at a temperature of 500° C. for 12 hours. However, this baking step may be eliminated by allowing the oxidized parts to stand in the open air under normal atmospheric conditions for a relatively long period of time, such as three months before using, this standing allowing any adsorbed hydrogen to be released from the parts.

To avoid the difficulty of adsorbed hydrogen referred to above, an alternative oxidizing process may be used comprising separate oxidizing steps for the metal disc and the chrome iron cap 1. For example, as shown in Figure 3, the oxidation of the chrome containing disc 7 may be simultaneous with the sealing of the glass tubing 5 to the cap 1. As shown in Figure 3, the inverted assembly including the cap 1 and disc 7 is supported over a gas flame 10, allowing the end of the tubing 5 to bear its own weight against the cap 1 and heating the cap and disc 7 for a time sufficient to seal the glass to the cap around the aperture 4. This operation simultaneously forms a relatively thin coating of greenish chromic oxide on the surface of the disc 7. Alternatively, the oxidation and sealing may be by pointed gas flames impinging the upper side of the cap 1 as disposed in Figure 3, allowing the heat to be conducted through the cap 1 and the disc 7 for oxidation of the disc. The necessary oxidation of the cap 1, especially around the edges thereof to provide a good seal to the glass tubing 3 may be performed by a ring-type burner which heats only the edges of the cap. I have found that a minimum of gas adsorption is produced by this method of oxidizing so that little if any gas such as hydrogen is available for diffusion into the envelope following exhaust.

I have referred to the use of chromium or a chrome alloy as the metal of the cathode foundation disc 7. The preferred material is a chromium nickel alloy having from 5 to 30 percent chromium by weight, the balance being nickel except for minor impurities such as silicon and manganese which do not appear to affect the operation of my phototube. A somewhat purer chromic oxide can be obtained by the use of the higher percentages of chromium. Although there may be some nickel oxide formed, especially when the oxidation is by a gas flame rather than by firing in moist hydrogen, this presence of nickel oxide seems to be immaterial inasmuch as the full advantages are obtained with both methods of oxidizing, the moist hydrogen method providing no nickel oxide but having the disadvantage of introducing hydrogen in the parts which must be removed by baking or long standing. Furthermore, the benefits of my invention are believed to accrue only from the use of the chromic oxide inasmuch as pure nickel foundations, oxidized and coated with antimony, are not as highly photosensitive as those containing the preferred range of chromium.

Following the formation of the cap and disc assembly and the sealing of the glass exhaust tubing 5 thereto, I seal the glass tubing 3 to the cap 1 to form an open-ended envelope providing an hermetic seal between the glass tubing 3 and the cap 1, thereby preventing leakage of air within the tube at this point during and following subsequent evacuation.

Following the above operation and in accord-

ance with my invention, I deposit a metal such as antimony on the chromic oxide film 8 to form a coating of antimony 9 as shown in Figure 2. My preferred method of providing a coating of antimony incorporates the use of apparatus such as shown in Figure 4. Referring to Figure 4, I insert the glass tubing 3 over a tubular or cylindrical open-ended shield 3a, the shield extending to within close proximity or slightly overlapping the foundation disc 7 on which the antimony is to be deposited. The shield 3a is preferably supported within a chamber or bell jar 11 capable of being evacuated. I also support opposite the disc 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 3a, I evacuate the bell jar 11 to a high vacuum, the residual air pressure preferably being less than 0.5 micron of Hg pressure and I then evaporate a sufficient quantity of antimony from the source 13 to provide the coating 9 of the desired thickness on the chromic oxide film 8. 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 9 is preferably less than 0.2 milligram per square centimeter of surface area exposed to the antimony coated coil 12 per minute, since I have found that a higher rate of condensation may be detrimental and form a nonuniform 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 disc 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 3a may be located radially around a centrally disposed source of antimony so that a number of cathodes may be processed simultaneously. Following the formation of the antimony coating 9, I remove the glass tubing 3 from the shield 3a 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 9. 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 9 provided the distance between the seal and the cathode, in Figure 1, is at least one-half inch and the cathode foundation is cooled during the sealing operation. To prevent excessive heating of the coating 9, I maintain cap 1 during the time the opposite cap 2 is sealed to the glass tubing 3 relatively cool. 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 disc 7, although the member 15 or the cap 1 itself may be artificially cooled such as by a blast of cold air. 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 9, 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 cap to better advantage.

It will be noted that in accordance with my teaching contained in my original application, the foundation bearing the antimony coating 9 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 percent relative humidity at 25° C. which corresponds to a water vapor concentration in the atmosphere equivalent to eight 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 9 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 9 to provide a photocathode having a very high sensitivity to light. Following the baking, the tabulation may be tipped off and the tube removed from the pump and rebaked at 160° C. for 20 minutes and aged in a manner described in my copending application Serial No. 342,199 filed June 25, 1940, to stabilize the photo-electric 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 9 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.

I do not wish to be limited to any particular theory explaining the improved operation of my phototube but I believe two factors may be of importance. First, the oxide film may serve as a heat insulator so that the antimony film is maintained at a lower temperature during the baking steps. Such lower temperature may result in less vaporization of the coating and favor the formation of an alkali metal-antimony combination which is more highly photoemissive. In addition, it may be that the chrome oxide supplies a small amount of its adsorbed oxygen to the photosurface thereby increasing the photoemission as disclosed in my copending application Serial No. 342,199, filed June 25, 1940.

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 in the tube 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 an envelope, a cathode foundation in said envelope, a coating of an oxide of chromium on said foundation and a coating on said chromic oxide coating comprising an alkali metal and an element selected from the group consisting of antimony, arsenic, and bismuth adapted to be photo-sensitized thereby.

2. A phototube comprising an envelope, a cathode foundation having an exposed surface within said envelope, a coating of chromic oxide on said foundation, an alkali metal containing coating of an element selected from the group consisting of antimony, arsenic and bismuth on said chromic oxide coating, and an anode having an exposed surface within said envelope to receive electrons from said alkali metal containing coating.

3. A phototube comprising an envelope having an anode and a cathode foundation therein, said cathode foundation including chromium, an integral coating of an oxide of chromium on said foundation and a film of alkali metal containing antimony on said oxide coating.

4. A phototube comprising an envelope, a cathode foundation having a surface exposed within said envelope, said foundation containing chromium, a coating of chromic oxide on said foundation, a film of alkali metal treated antimony on said foundation, and an anode to receive electrons from said alkali metal treated coating.

5. A phototube comprising an envelope, a metal member comprising 5 to 30% chromium by weight in said envelope, a coating on said metal member comprising an alkali metal and antimony and an anode to receive electrons from said coating.

6. A phototube comprising an envelope of transparent insulating material, a metal cap sealed to and closing one end of said tubular envelope, a coating of an alkali metal treated element selected from the group consisting of antimony, arsenic and bismuth adjacent said cap

and an intermediate film of an oxide of chromium between said cap and said coating to provide thermal insulation between said cap and said coating.

7. A phototube comprising a cylindrical glass envelope of predetermined length, a metal closure cap hermetically sealed to each end of said envelope, a chromium containing metal member adjacent one of said caps, an integral coating of chromic oxide on said metal member, a film of an element selected from the group consisting of antimony, arsenic and bismuth on said coating, said film being removed from the other of said caps by a distance of at least three-quarters of an inch whereby the sealing of said opposite cap to said glass envelope does not injure said film and an alkali metal deposited on said film to render said film photo-sensitive.

8. A photocathode comprising an oxidized chromium containing member and an alkali metal treated coating of an element selected from the group consisting of antimony, arsenic and bismuth.

9. A photocathode comprising an oxidized metal member having a chromium content of from 5 to 30% by weight and an alkali metal treated antimony coating on said member.

10. A photocathode comprising a foundation of nickel and chromium, a film comprising greenish chromic oxide on said member and a coating of alkali metal treated antimony on said chromic oxide film.

11. The method of manufacturing an electron emissive electrode comprising forming a greenish oxide on a chromium containing metal member, coating said oxide with a film of an element selected from the group consisting of antimony, arsenic and bismuth, and depositing an alkali metal on said film of said element.

12. The method of manufacturing a phototube which comprises oxidizing a chromium containing foundation, supporting said foundation adjacent one end of an open-ended tubular glass envelope, depositing an element selected from the group consisting of antimony, arsenic and bismuth through the open end of said envelope and upon the oxidized surface of said foundation, sealing a metal cap to the opposite end of said envelope, evacuating said envelope, and depositing an alkali metal on the element of said group on said oxidized surface to photosensitize said element.

13. The method of manufacturing a phototube having two metal closure caps separated by a tubular insulating member comprising oxidizing a chromium containing surface supported by one of said caps to a greenish color, sealing said cap to one end of said tubular member with the oxidized surface extending inwardly of said member, depositing a film of antimony on said oxidized surface, sealing the other cap to the other end of said member without heating said antimony film to a temperature at which it becomes oxidized, exhausting the envelope formed by said caps and said member and sensitizing said antimony film with an alkali metal.

14. The method of manufacturing a phototube having two metal closure caps separated by a tubular insulator comprising affixing a metal member containing chromium to a metal cap, oxidizing said member to provide a film of chromic oxide thereon, sealing said cap to one end of said insulator with the oxidized member within said insulator, depositing a film of antimony on the oxidized surface of said member, then sealing

the other cap to the other end of said insulator without heating the deposited film to a temperature at which it becomes oxidized, exhausting the envelope formed by said insulator and closure caps and sensitizing said film with an alkali metal.

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