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METHOD OF MANUFACTURING PHOTOELECTRIC TUBES

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Fig. 1

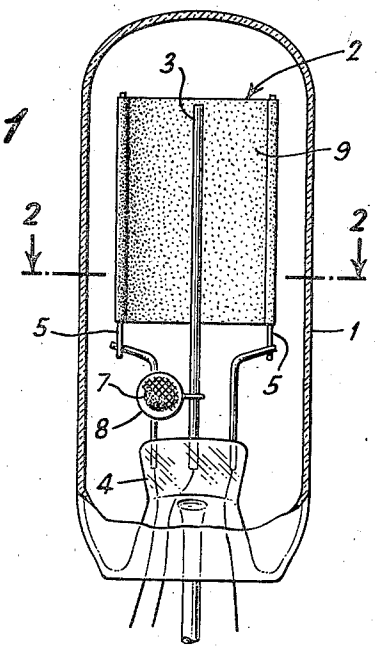
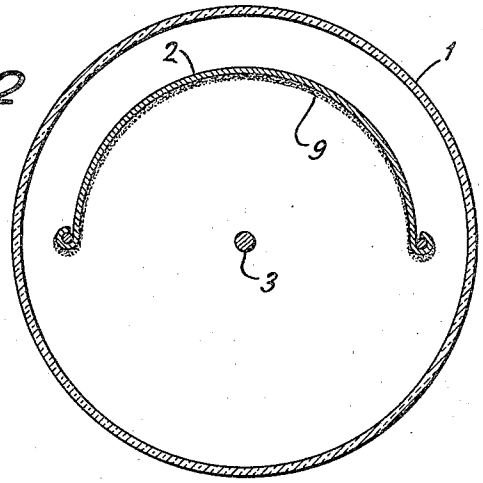


Fig. 2



INVENTORS
ROBERT B. JANES AND
ALAN M. GLOVER

BY Charles McClain
ATTORNEY.

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METHOD OF MANUFACTURING PHOTOELECTRIC TUBES

Robert B. Janes, Verona, and Alan M. Glover, East Orange, N. J., assignors to Radio Corporation of America, a corporation of Delaware

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16 Claims. (Cl. 250—165)

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Our invention relates to photoelectric tubes and their method of manufacture and particularly to tubes incorporating metals of the second sub-group of the fifth group of the periodic system photosensitized with metals of the alkali metal group.

Several types of phototubes are known including those of the silver-silver oxide-caesium type but such tubes have relatively high sensitivity in the infra-red region of the spectrum but low sensitivities in the visible range and especially in the blue portion of the visible spectrum. In addition this type of phototube is difficult to manufacture and manufacturing cost is relatively high. Attempts have been made to modify the sensitivity of such tubes such as by processing the silver-silver oxide-caesium surface in such a manner that it is deficient in caesium. Although with such processes the infra-red sensitivity is reduced and the blue sensitivity increased, the largest part of the sensitivity remains in the red portion of the spectrum. While rubidium has been substituted in this type of tube for the caesium to obtain higher sensitivity in the visible spectrum, the sensitivity to incandescent light is fairly low being at best 15 micro-amperes per lumen. Higher sensitivity can be obtained only by permitting a higher infra-red response. Notwithstanding improved sensitivity to visible light, the processing is quite involved and expensive.

It is an object of our invention to provide a phototube having higher photosensitivity than the tubes made heretofore. It is also an object to provide a tube having exceptionally high photosensitivity to blue light and a method wherein the processes of manufacturing such a tube are simplified and controllable to a high degree of accuracy, thereby assuring good reproducibility in the manufacture of a large quantity of tubes, and it is a still further object to provide a manufacturing process for producing such tubes consisting of a minimum number of readily controlled steps.

In accordance with our invention we provide a cathode foundation on which we deposit antimony or another metal of the second sub-group of the fifth group of the periodic system at a predetermined rate in a rarefied atmosphere to provide a metal film of critical thickness, following which the cathode foundation with its film of metal is sealed in an envelope, exhausted and baked at a critical temperature for a sufficient length of time to produce certain desired color changes following which the cathode film is subjected to alkali metal vapor, such as caesium

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vapor, whereupon the tube is again baked and aged to be ready for use.

These and other objects, features and advantages of our invention will be apparent when taken in connection with the following description of our invention and the accompanying drawing in which:

Figure 1 is a longitudinal view of a tube made in accordance with our invention; and

Figure 2 is an enlarged cross section of the tube shown in Figure 1 taken along the lines 2—2.

Referring to the drawing we provide an envelope 1 enclosing an electrically conducting foundation or cathode 2 on which a photosensitive surface is formed and an anode 3 exposed to the photosensitive surface so that it may receive electrons which are liberated from the cathode under the influence of light. The cathode 2 and anode 3, which are made of nickel or other base metal, are preferably supported by a stem or press 4 preferably of lead glass and in which the current carrying leads or support rods 5 to the cathode and the anode are sealed. The tube shown in the drawing is provided with a tubulation 6 through which the tube may be evacuated and a source of caesium or other alkali metal is provided within the bulb 1 or in an adjacent interconnecting envelope; although we prefer to provide a quantity of caesium bearing compound such as an activating pellet 7 which is in good thermal contact with a metal tab 8 so that caesium may be liberated from the pellet by suitable heating treatment.

In accordance with one teaching of our invention a metal such as antimony is deposited in vacuo on a cathode foundation 2 of nickel or other base metal prior to sealing the cathode foundation within the bulb 1 and so deposited that the antimony film 9 is applied by vaporizing the antimony and condensing the vapor on the cathode foundation at a rate not exceeding 0.1 milligram per square centimeter per minute. We have found that when depositing antimony on a foundation, it is necessary to limit the rate at which the antimony is deposited to obtain a surface which when sensitized with an alkali metal such as caesium will result in a high sensitivity to light in the blue portion of the spectrum. Cathodes prepared with the antimony deposited at a rate greater than 0.2 milligram per square centimeter have resulted in tubes of poor sensitivity. This condition is indicated by a spotty appearance of the deposited film during the final steps of the deposition. The antimony employed should be pure for we have found that small

amounts of impurities such as lead, tin, copper, and iron may reduce the final sensitivity as much as two to one. We have likewise found that the deposited thickness is quite critical, that while tubes utilizing cathodes with relatively thin films of antimony may be sensitized with a smaller than normal amount of alkali metal and similarly tubes having thicker antimony films may be sensitized with an excessive amount of alkali metal, such tubes are nevertheless deficient in sensitivity. Thus, tubes having an antimony film thickness believed to be in the range of 900 to 1100 angstroms may be sensitized to obtain exceptionally high photosensitivity, this being as high as 85 micro-amperes per lumen when illuminated from a tungsten light source operating at 2870° K.

As an example of one preferred method of depositing the antimony a plurality of foundations may be coated simultaneously in a separate evacuated chamber or bell jar which is free of deleterious materials such as grease or hydrocarbons. The foundations may be formed to the arcuate shape shown in Figure 2, assembled with the side rods 5 and following thorough cleaning by washing in ether are mounted in a vertical position on a metal ring, 7 inches in diameter, so as to face the center of the ring. Twenty-four cathode foundations of a size particularly suitable for phototube use, each having a front surface area of 3.9 square centimeters, may be mounted around the ring with their concave sides toward the center. A conical insulated coil of refractory metal wire such as tungsten containing the antimony to be vaporized is placed in the center of the ring and a weight of 120 to 160 milligrams of antimony is completely vaporized over a period of 1.2 to 1.6 minutes to provide the proper thickness of the antimony film 9. The tungsten coil is preferably insulated with sintered aluminum oxide to prevent alloying of the antimony with the tungsten which we have found produces non-uniformities in the weight of antimony vaporized as well as poisoning of the antimony. During the vaporization process the residual pressure of the evacuated envelope may be from 0.1 to a few microns, as long as the residual atmosphere is air. We have found that if the residual pressure is above 0.5 micron, antimony is deposited on the rear surface of the convex side of the cathode which then becomes spotted upon subsequent treatment. The above weights of antimony result in a calculated weight of 0.12 and 0.16 milligram per square centimeter when deposited from a source 3½ inches from the foundations and the color of the deposited film is a light steel gray. An excessively thick film of antimony of the order of 25% thicker than that resulting from the above upper weight limit tends to break up during later treatment leaving portions of the foundation exposed. Since the cathode foundations, during condensation of antimony thereon, are arcuate shaped with the concave side toward the evaporating source the thickness of the deposited antimony near the center of the cathode is greater than at the edges where the thickness is substantially zero. The desired thickness corresponding to 0.12 to 0.16 milligram per square centimeter is the proper thickness over the central portion of the cathode and may vary somewhat due to the spherical propagation of antimony vapor from the evaporating source. The very thin film adjacent the edges and near the side rods 5 is conducive to more accurate processing and will be referred to below.

During the construction of the first phototubes made in accordance with our invention, it was believed that subjecting the antimony coated cathodes to the atmosphere would injuriously affect the antimony coating during the time between the removal of the cathodes from the bell jar or enclosure referred to above and sealing in of the cathodes within the phototube envelopes. However, we have exposed the coated cathodes to normal atmospheric conditions for a period of many days without being able to observe any difference in the final product with respect to tubes wherein the antimony was not subjected to the atmosphere. However, we have found that the relative humidity of the atmosphere to which the coated cathodes are subjected should be low. Thus we have found this method unsatisfactory if the cathodes are subjected to high relative humidities such as humidities of over 80% at 25° C. We, therefore, prefer to maintain the humidity below a water vapor concentration 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, as we have been unable to find any trace of antimony oxide on the antimony film following such treatment. However, we do not fully understand the action of high humidity in producing unsatisfactory results, but this may be due to the formation of an oxide film on the thin film of antimony.

Following the deposition of antimony film 9 the cathodes are sealed into individual envelopes such as the bulb 1 with the concave side facing the anode 3 and the envelopes exhausted. No oxygen, whatsoever, is introduced within the tube during the exhaust cycle or subsequent thereto and in fact the introduction of oxygen substantially ruins the sensitivity of the completed tube. The tube is then baked to remove occluded gases and in accordance with our invention a small portion of the antimony film is vaporized to provide a clean antimony surface. In accordance with this teaching of our invention we control the baking step both with respect to temperature and time to produce a very slight vaporization of a portion of antimony and continue the baking until a particular color is obtained, this color being a very light pink. This color change from a steel gray to a just perceptible pinkish color may be due to some chemical reaction or to a new and clean surface being formed on the antimony film. The temperature range and the time of baking is very critical, in fact, we have used two ovens apparently operating at the same temperature and the tubes from one oven had sensitivities as high as 60 to 70 micro-amperes per lumen whereas tubes from the other oven had sensitivities of only 30 to 40 micro-amperes per lumen. Thus, while the two ovens were apparently operated at the same temperature, difference in construction of the ovens resulted in an incorrect tube baking temperature and the rate of heating the cathodes was also different than in the oven producing tubes of high sensitivity. While both time and temperature are critical features in the production of the very slight pinkish color which is desired, a somewhat lower temperature for a slightly longer time produces an equivalent color change although with an oven temperature of 275° to 325° C., preferably centered at 300° C., the color change appears after the tubes are

baked for one-half hour. The data given above are for tubes raised from room temperature by lowering the oven after it has reached the indicated temperature over the tubes allowing it to remain for the time indicated. The color change appears first at the edges of the cathode foundation apparently due to the conduction of heat to the cathode by the support side rods and serves as an excellent indication of the degree of baking. Thus if the coating of antimony is thinner at the edges of the cathode foundation the change in color from a light steel gray to a gray with a pinkish tinge occurs first at the thin edges and the baking following the appearance of this color change should be discontinued immediately. Continued heating either at a higher temperature or for a prolonged time is detrimental as indicated above and may be evidenced by the slightly pinkish color deepening into a red for which the final results are very poor. On the other hand, a bake-out temperature of less than 275° C. results in insufficient removal of the residual or occluded gases in the envelope and electrode structure.

We have found a higher average sensitivity is obtainable, if prior to sealing the stems to the envelopes, the envelopes are first baked at a temperature of 450° C. for a period of one-half hour followed by sealing-in of the electrode and rough exhaust of the tube within as short a time as possible after this baking. Following the baking the caesium bearing compound such as the pellet 7 is flashed to liberate caesium within the envelope 1. During the liberation of caesium within the envelope we maintain the temperature of the envelope and electrode structure at such a temperature as to cause an alloying of the alkali metal with the antimony film 9. The temperature to produce such alloying may vary over wide limits, extending from room temperature up to 200° C. and since the cathode is within the envelope, this cathode is maintained at substantially the same temperature. Immediately upon the liberation of caesium the photosensitivity of the cathode increases, such photosensitivity being substantially non-existent prior to liberation of caesium and such increase is observed even when the bulb 1 is maintained at room temperature. Following the liberation of caesium within the tube, the tube is baked in an oven at a temperature of 150° C. to 170° C. until the photosensitivity has reached a maximum. Some tubes reach a maximum photosensitivity following a baking of a few minutes, whereas other tubes require baking for several hours. Continued baking after maximum sensitivity has been obtained does no harm to the tubes so that we prefer to seal off the bulb 1 from the exhaust system so that a large quantity of tubes may be baked together in a large oven for a time sufficient for all the tubes to attain maximum photosensitivity.

It will be noted above that we prefer to utilize an antimony film thickness or coating weight having rather narrow limits. This antimony film when treated in accordance with our invention by baking, prior to liberation of caesium, to a point at which the pinkish color just appears followed by sensitizing with caesium without the oxidation taught by the prior art has produced tubes with a maximum photosensitivity of 85 micro-amperes per lumen to tungsten light at color temperatures of 2870° K. This is a sensitivity far in excess of that obtained by processes known in the art including a step or steps of oxidizing the antimony film or antimony caesium

alloy. Since the thickness of antimony film is critical, it is logical that the amount of caesium used is relatively critical. A deficiency of caesium gives a bluish appearing cathode surface of very low sensitivity after baking whereas by increasing the amount of caesium and baking the color changes to a greenish blue and the sensitivity rises tenfold. We have found that this high sensitivity can be obtained with the use of a pellet 7 weighing 20 milligrams comprising by weight two parts caesium chromate, eight parts tantalum powder and one part aluminum powder.

As mentioned above the stem or press 4 may be of lead glass. The use of such glass apparently reduces the amount of free caesium in the finished tube during the final baking period. Considerable difficulty has been experienced in manufacturing gas filled phototubes incorporating an antimony-alkali metal photocathode. We have found that if an inert gas such as argon is introduced within the envelope during or just prior to the liberation of the alkali metal, favorable results may be obtained. It appears that the sensitized antimony film is very sensitive to foreign substances but if the alkali metal such as caesium is present in vapor form after the introduction of the inert gas the advantages of gas ionization during tube operation may be obtained. This gas may be introduced either just before flashing of the caesium compound or while the caesium is still in vapor form. Thus the caesium may be deposited on the interior walls of the envelope by maintaining the walls at a relatively low temperature such as 30 to 40° C. whereupon the inert gas may be introduced followed by the final baking step to drive the caesium to the antimony coated cathode foundation. Tubes made in accordance with this teaching of our invention have high sensitivity and far better life than tubes made in accordance with an adaptation of the known process wherein the inert gas is introduced as a final step.

While we have described our invention in connection with the use of antimony, it is to be understood that we do not wish to be limited to this particular metal, since we have found arsenic and bismuth to be satisfactory as an equivalent of antimony. Therefore, while we have indicated the preferred embodiments of our invention of which we are now aware and have also indicated only certain specific applications for which our invention may be employed, it will be apparent that our invention is by no means limited to the exact forms illustrated or the use indicated, but that many variations may be made in the particular structure used and the purpose for which it is employed without departing from the scope of our invention as set forth in the appended claims.

We claim:

1. The method of manufacturing a photosensitive electrode which comprises depositing a film of antimony on an electrically conductive foundation in a non-oxidizing atmosphere, subjecting said foundation and said film to the atmosphere, sealing said foundation bearing said film in an envelope, evacuating said envelope to provide a non-oxidizing atmosphere within said envelope, depositing an alkali metal on said film and baking said film to photosensitize said film without first forming an oxide on said film.

2. The method of manufacturing a photosensitive electrode which comprises depositing in a non-oxidizing atmosphere a film of antimony on an electrically conductive foundation having an

extended area at a rate less than 0.2 milligram per square centimeter per minute, subjecting said foundation and said film to the atmosphere, sealing said foundation bearing said film in an envelope, evacuating said envelope to provide a non-oxidizing atmosphere within said envelope, heating said foundation and film at a temperature between 275° C. and 325° C., and depositing an alkali metal on said film to photosensitize said film without first forming an oxide on said film.

3. The method of manufacturing a photosensitive electrode which comprises supporting an electrically conductive foundation having an extended area in a non-oxidizing atmosphere, depositing a film of antimony on said foundation at a rate not exceeding 0.1 milligrams of antimony per square centimeter per minute, subjecting said foundation and said film to the atmosphere, sealing said foundation bearing said film in an envelope, evacuating said envelope to provide a non-oxidizing atmosphere within said envelope, baking said envelope at a temperature between 275° C. and 325° C. until said film acquires a pinkish color, and depositing an alkali metal on said film to photosensitize said film.

4. The method of manufacturing a photosensitive electrode which comprises supporting a metal foundation in an evacuated envelope, depositing a film of antimony on said foundation at a rate less than 0.2 milligram per square centimeter per minute until the thickness of said film is equivalent to a weight of 0.12 to 0.16 milligram per square centimeter area of said foundation, baking said film in a non-oxidizing atmosphere until said film acquires a pinkish color, depositing an alkali metal on said film, and baking said film to photosensitize said film.

5. The method of manufacturing a photosensitive electrode which comprises supporting an arcuate electrically conductive foundation in an evacuated chamber with its concave side facing a source of antimony, depositing antimony on the concave surface of said foundation to form an antimony film thinner at the edges of said arcuate foundation than in the center thereof, subjecting said foundation and said film to the atmosphere, sealing said foundation bearing said film in an envelope, evacuating said envelope to provide a non-oxidizing atmosphere within said envelope, baking said envelope and foundation until the thinner edges of said film acquire a pinkish color, depositing an alkali metal on said film and baking said envelope and foundation to photosensitize said film.

6. The method of manufacturing a gas filled phototube which comprises depositing a film of antimony on an electrically conductive foundation in a non-oxidizing atmosphere, baking said foundation until said film acquires a pinkish color, liberating alkali metal within said envelope, introducing an inert gas within said envelope while said alkali metal is in vapor form, and baking said envelope and foundation to photosensitize said film of antimony.

7. The method of manufacturing a gas filled phototube which comprises depositing a film of antimony on a metal foundation, sealing said foundation bearing said film in an envelope, evacuating said envelope, baking said foundation until a portion of said film evaporates and acquires a pinkish color, liberating alkali metal within said envelope, admitting an inert gas into said envelope while said alkali metal is in vapor form and baking said envelope to photosensitize said antimony film.

8. The method of manufacturing photosensitive devices which comprises supporting a plurality of metallic members in an envelope, evacuating the envelope, forming a film of antimony on each of said members, removing the members from said envelope and into an atmosphere containing less water vapor than that or an atmosphere having 80% relative humidity at 25° C., sealing each of said members in an individual envelope, evacuating each of said individual envelopes and subjecting the metallic member in each envelope to the vapor of an alkali metal prior to any step of oxidation of the film of antimony to photosensitize the film of antimony.

9. The method of manufacturing a plurality of photosensitive devices which comprises supporting a plurality of metallic members in an envelope, evacuating the envelope, forming a film of antimony of a thickness corresponding to a weight of 0.12 to 0.16 milligram per square centimeter on each of said members, removing the members from said envelope, sealing each of said members in an individual envelope, evacuating each of said individual envelopes, baking each of said envelopes until the said films assume a pinkish color and subjecting the metallic member in each envelope to the vapor of an alkali metal prior to any oxidation of the film of antimony to photosensitize the film of antimony.

10. The method of manufacturing a plurality of photosensitive devices which comprises supporting a plurality of arcuate metallic members in an envelope with their concave surfaces facing a source of antimony, evacuating the envelope, forming a film of antimony on the concave surface of each of said members such that the film thickness is less adjacent two parallel edges than intermediate thereof, removing the members from said envelope, sealing each of said members in an individual envelope, evacuating each of said individual envelopes, evaporating a portion of the antimony from the foundation in each of said envelopes by baking and continuing said baking until said films acquire a pinkish color adjacent the said edges thereof, subjecting the metallic member in each envelope to the vapor of an alkali metal, and baking each of said envelopes to photosensitize said metallic members.

11. The method of manufacturing photosensitive devices which comprises supporting a plurality of metallic members in an envelope, supporting within said envelope a source of antimony to be vaporized, evacuating the envelope, vaporizing a quantity of antimony to form a film of antimony on each of said members, subjecting said members to air having a relative humidity not greater than 80 per cent at 25° C., sealing each of said members in an individual envelope, evacuating each of said individual envelopes and subjecting the metallic member in each of said envelopes to the vapor of an alkali metal prior to any oxidation of the film of antimony to photosensitize the film of antimony.

12. The method of manufacturing a plurality of photosensitive devices which comprises the steps of simultaneously coating a plurality of electrically conductive cathode foundation members with a film of antimony in an evacuated chamber, removing the said members from the chamber and subjecting said members to air containing less than eight grains of water vapor per cubic foot of air, sealing said members in a plurality of envelopes, evacuating the envelopes and depositing alkali metal on the exposed surface of the film on each member to photosensitize the

film while said film remains in an unoxidized state.

13. The method of manufacturing a plurality of photosensitive devices which comprises the steps of simultaneously coating a plurality of electrically. conductive cathode foundation members with a film of antimony in an evacuated chamber, removing the said members from the chamber and subjecting said members to air containing less than eight grains of water vapor per cubic foot of air, sealing said members in a plurality of envelopes, evacuating the envelopes, baking said envelopes until the said films of antimony acquire a pinkish color, and depositing alkali metal on the exposed surface of the film on each member to photosensitize the film without subjecting said film to an oxidizing atmosphere.

14. The method of manufacturing a plurality of photosensitive devices which comprises the steps of simultaneously coating a plurality of arcuate electrically conductive cathode foundation members with a film of antimony of increasing thickness from two opposite edges toward the center of said members, removing the said members from the chamber and subjecting said members to air containing less than eight grains of water vapor per cubic foot of air, sealing said members in a plurality of envelopes, heating the said edges of said foundation members in a non-oxidizing atmosphere at a rate faster than the centers of said members, discontinuing the heating of said members following the appearance of a pinkish color adjacent said edges and prior to the appearance of a deep red over the surface of said films, and depositing alkali metal on the exposed surface of said films to photosensitize said films.

15. The method of manufacturing an electron emissive electrode which comprises the steps of depositing a film of a metal selected from the second sub-group of the fifth group of the periodic system on an electrically conductive foundation in a non-oxidizing atmosphere, subjecting said foundation bearing said film to the atmosphere without materially oxidizing said film, sealing said foundation bearing said film in an envelope, evacuating said envelope to provide a non-oxidizing atmosphere exposed to said film, depositing an alkali metal on said film and baking said foundation and said film to finally sensitize said film without forming an oxide on said film intermediate the said steps of sealing said foundation in said envelope and the final sensitization of said film.

16. The method of manufacturing an electron emissive electrode which comprises the steps of depositing in a non-oxidizing atmosphere a film of a metal selected from the second sub-group of the fifth group of the periodic system on an electrically conductive foundation, subjecting said foundation bearing said film to a normal room atmosphere containing less water vapor than that represented by a relative humidity of 80% at 25° C., sealing said foundation bearing said film in an envelope, evacuating said envelope to provide a non-oxidizing atmosphere exposed to said film, depositing alkali metal on said film and baking said foundation and film to finally sensitize said film without intermediately oxidizing said film between the steps of evacuating said envelope and finally sensitizing said film.

ROBERT B. JANES.
ALAN M. GLOVER.