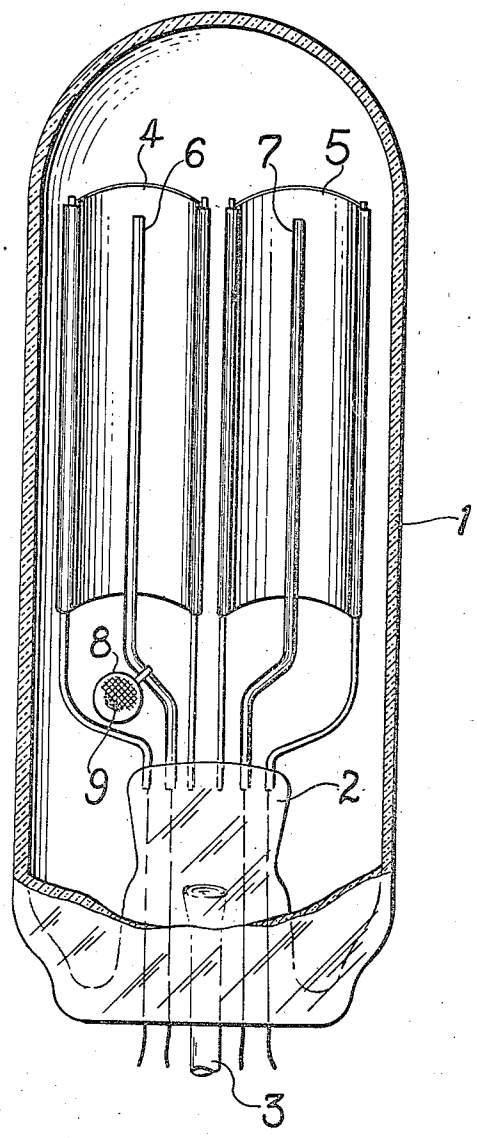
Dec. 24, 1946. R. W. ENGSTROM 2,413,222

PHOTOELECTRIC TUBE AND METHOD OF MANUFACTURE

Filed May 29, 1943



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Patented Dec. 24, 1946

2,413,222

UNITED STATES PATENT OFFICE

2,413,222

PHOTOELECTRIC TUBE AND METHOD OF MANUFACTURE

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Application May 29, 1943, Serial No. 489,001

8 Claims. (Cl. 250—165)

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My invention relates to photoelectric tubes and their methods of manufacture and particularly to tubes incorporating within a single envelope a photoelectric cathode of the alkali metal-silver-silver oxide type as well as a cathode of a metal of the second sub group of the fifth group of the periodic system photosensitized with a metal or metals of the alkali metal group.

The photoelectric characteristics of photo-cathodes comprising an oxidized silver foundation sensitized with an alkali metal are well known, the spectral sensitivity characteristics of such cathodes being high in the red to infra-red portion of the spectrum. Similarly, the characteristics of a photo-cathode having an element selected from the group consisting of antimony, arsenic and bismuth sensitized with an alkali metal are likewise well known to have spectral sensitivity characteristics in the blue and violet regions of the spectrum. However, it has not been possible to combine these two types of cathodes within a single envelope and obtain the optimum photoelectric sensitivity from each cathode because the processing of one has been incompatible with the processing of the other cathode. It is very desirable that highly sensitive cathodes of these two types be incorporated in a single envelope for use in colormetric applications and uses where is is desired to provide a wide spectral sensitivity extending over the yellow-green and blue-violet portions of the spectrum.

It is an object of my invention to provide a photo-tube having an overall spectral sensitivity extending from the yellow-green to the blue-violet portions of the spectrum. It is another object to provide a photo-tube wherein the optimum characteristics of high sensitivity are obtained over a broad portion of the photo-electric spectrum. It is a further object to provide a photo-tube and a method of manufacture wherein photo-cathodes having different spectral sensitivity may be processed simultaneously within a single envelope to optimum photosensitivity; and it is a still further object to provide a method of manufacturing photo-tubes of the type described wherein the processing of one photo-cathode is compatible with the processing of another photo-cathode having different spectral characteristics.

In accordance with my invention I provide a plurality of cathode foundations with one or more anode electrodes within a single envelope; and I provide one foundation either of silver or of a silver coated base metal and the other foundation with a coating of antimony, arsenic or bismuth. I then oxidize the silver or silver coating of the one foundation to a predetermined extent and liberate within the envelope an alkali metal of a quantity determined by such oxidation to provide a definite ratio of alkali metal to the metal, such as antimony, arsenic or bismuth on the other foundation. More particularly, I have found in accordance with my invention that optimum photosensitivity may be obtained from an alkali metal treated oxidized silver foundation as well as from an alkali metal treated antimony, arsenic or bismuth coated foundation provided the thickness of oxide of the silver foundation is maintained within relatively narrow limits, the limits being determined with respect to the ratio of the arsenic or bismuth to alkali metal.

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I have referred above to a silver or silver coated foundation and it will be appreciated that either type is interchangeable with the other, and likewise that antimony, arsenic or bismuth may be used interchangeably as a coating for the other cathode foundation. Consequently, I will refer in the following description of my invention to a silver cathode and to an antimony coated cathode, it being understood that arsenic or bismuth may be substituted either in whole or in part for the antimony and that a silver plated base metal may be substituted for the silver foundation.

The objects referred to above as well as other objects, features and advantages of my invention will become apparent when taken in connection with the accompanying drawing wherein the single figure is an enlarged longitudinal view of a photo-tube made in accordance with my invention.

Referring to the drawing, one type of tube made in accordance with my invention comprises an envelope 1 of lime glass having a stem or press member 2 of lead glass provided with the conventional exhaust tubulation 3 and supporting thereon within the envelope 1 two cathode foundations 4 and 5 and, in addition, one or more anodes such as the anodes 6 and 7. While I have shown two anodes, a single anode may be used if desired; and furthermore, while I have shown connecting leads to each of the electrodes within the envelope, it will be appreciated that this showing is merely for greater flexibility in use. Thus the two cathodes may be internally connected together and provided with a single lead either with the plurality of anodes or with a single anode. Such alternate constructions are merely for greater flexibility in use, the structure shown being adapted to a greater number of applications wherein the use of separate cath-

odes and anodes is desired. In addition to the structure described, I provide an activator retainer 8 partially enclosing a source 9 of alkali metal for use in photoelectrically activating the photo-cathodes.

As will be appreciated from the procedure outlined below, the processing of the cathodes is dependent upon the cathode surface area with respect to the amount of alkali metal liberated within the envelope. I have made satisfactory tubes wherein the area of the cathodes exposed to the respective anodes was 6½ square centimeters in combination with a caesium activator weight of 47 to 53 milligrams, the composition of the activator being one part powdered caesium dichromate to two parts of powdered silicon by weight.

In accordance with my invention, I provide the base of one of the cathodes such as the cathode 4 of silver which, following assembly within the envelope 1, is oxidized such as by a glow discharge developed between the cathode 4 and the anode 6 in a rarefied oxygen containing atmosphere as is customary in the production of conventional silver-silver oxide-alkali metal cathodes, although as more particularly described hereinafter, I control this oxidizing step to provide a critical thickness of oxide on the cathode 4. Further, in accordance with my invention, I provide the cathode 5 of an antimony coated base metal such as nickel, although in accordance with the teachings of R. B. Janes in his application Serial No. 481,246, filed March 31, 1943, the cathode 5 foundation may be of an antimony coated chromium-nickel alloy which is oxidized to provide a film of chromic oxide as a base for the antimony. Prior to the assembly of the foundation for the cathode 5 within the envelope 1, I coat the foundation with an element such as antimony preferably by supporting the foundation in an evacuated chamber and condense antimony from the vapor phase thereon at a relatively low rate, preferably not exceeding 0.1 milligram of antimony per square centimeter per minute, thereby providing a uniform coating of antimony over the surface of the foundation to be sensitized. During the vaporization process, care should be exercised that the antimony is not deposited at a rate greater than approximately 0.2 milligram per square centimeter of intended sensitive surface area per minute inasmuch as a spotty appearance is produced which is inimical to further optimum processing. I have also found that the thickness of the deposited antimony is quite critical in a tube incorporating two cathodes of the type described and that this thickness should be controlled in accordance with the optimum limits of oxide coating on the cathode 4. Thus, in accordance with my invention, I provide an antimony film thickness of 900 to 1100 angstroms as calculated from the bulk density of the quantity used in combination with a silver cathode oxidized to provide an oxide having a thickness directly related to the thickness of the antimony coating.

The antimony coating, as indicated above, is deposited prior to the assembly of the cathode 5 in the envelope 1, the preferred thickness of 900 to 1100 angstroms being obtained by vaporizing a predetermined weight of antimony. Preferably a number of cathode foundations are processed simultaneously, being supported at equal distances from a source of the antimony vapor such as a filament coated with the antimony which may be heated allowing substantially

straight line propagation of antimony vapor to the cathode foundations. This vaporization is preferably performed in a vacuum wherein the residual pressure is less than 0.5 micron. To provide an antimony film thickness referred to above, I vaporize a weight of antimony of from 120 to 160 milligrams over a period of from 1.2 to 1.6 minutes. These 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. This amount of antimony when deposited as a film on the foundation has the appearance of a light steel gray color.

The foundation for the cathode 4 is cleaned such as by immersion in nitric acid followed by washing in distilled water and I then support the two cathodes from the press 2 and seal the structure within the envelope 1 whereupon the envelope is evacuated through the tubulation 3 and the resulting tube baked at a temperature of 250 to 300° C. to remove occluded gases from the envelope and electrode structures. Baking at this temperature for a period of 20 minutes to one-half hour is usually sufficient to remove the occluded gases following which, after the tube is allowed to cool, I introduce oxygen to a pressure of approximately 1.5 millimeters for the purpose of oxidizing the surface of the silver cathode 4. This oxidation step in accordance with my invention is performed by developing a glow discharge between the cathode 4 and the anode 6. The intensity and duration of the glow discharge is controlled to provide a predetermined color change of the cathode 4 when viewed by reflected light from a substantially white light source.

Preferably the cathode 4 is intermittently made negative at a potential of about 500 volts with respect to the anode 6, the glow discharge being maintained for a very short period, such as one-fourth second so that the color change can be observed. No more than two such pulses per minute is desirable to prevent excess heating of the cathode. When oxidizing the silver cathodes of a number of tubes, each cathode-anode combination may be pulsed twice in sequence, the cathodes being allowed to cool during the partial oxidation of the succeeding cathodes returning for additional partial oxidation of the first tube cathode and repeating this procedure until the desired color is obtained. During the entire oxidizing process the cathode 5 and anode 7 are left disconnected from any circuit, that is, the antimony coated cathode and associated anode are allowed to float with respect to all other energized electrodes in the tube to prevent oxidation of the antimony.

Prior to oxidation, the cathode 4 has a characteristic silver color, that is, a relatively bright mat finish such as obtained by the cleaning process in nitric acid. During the oxidation process the cathode 4 passes through a series of colors, the color first appearing being yellow, followed by the colors red and blue completing a first series of colors, and yellow, red and green comprising a second series. If this oxidation is continued, a third reddish color somewhat darker than the second red, followed by a darker green to black is produced, although I terminate the oxidation process prior to the attainment of these latter colors. Preferably, I terminate the oxidation process in the second series of colors and preferably between the second yellow and second red colors, to provide a thickness of oxide compatible with the thickness of antimony coating on the cathode 5 and compatible with the quan-

tity of alkali metal such as caesium which is necessary to provide optimum photosensitivity, both in the yellow-green portion of the spectrum for the cathode 4 and in the blue-violet portion for the cathode 5.

Following the oxidation of the cathode 4 to within the range of the second green and blue colors I again evacuate the envelope removing the residual oxygen and vaporize an alkali metal within the envelope. This is preferably done from a caesium containing pellet such as the pellet 9 contained within the envelope although an external caesium source, such as a small container connected with the envelope 1 by a tubulation, may be used. In accordance with my invention, I vaporize just sufficient alkali metal to provide an optimum photosensitivity for each of the cathodes with respect to the predetermined weight or thickness of antimony on the cathode 5 and the produced thickness of silver oxide on the cathode 4. I have found that a quantity of caesium corresponding to a weight ratio of from one to three parts of caesium to one part of antimony by weight produces optimum photosensitivity both for the antimony coating and the oxidized silver cathode. The caesium pellet 9 is preferably flashed while the envelope 1 is at or near room temperature, the caesium thus liberated being deposited on the inner wall of the envelope. I then bake the tube at a temperature preferably between 150° and 270° C. for a period of time such as from 3 to 20 minutes. During this baking operation the oxidized silver surface of the cathode 4 passes through a sequence of colors, these colors being black, brown, orange with brilliant brown spots, and dull yellow or straw color with dull brown spots. Continued baking produces a whitish color and I terminate the baking upon attainment of a range of colors between the orange and straw colors for best results. During the time the silver oxide changes to this range of colors the color of the antimony coated cathode changes from the steel gray color to a gun-metal blue which is a cathode color indicating high antimony sensitivity to blue light. Optimum photo surfaces may be produced simultaneously only by producing a condition lying between a deficiency of caesium and an excess of caesium. An excess of caesium is indicated when the oxidized silver surface has passed through the above sequency of colors during this baking to the characteristic straw color and high electrical leakage is apparent between either cathode and the anode or anodes. Following this baking step to the range of colors given above the proper amount of caesium is indicated when the resistance between leads through the stem press is of the order of 30,000 megohms per millimeter of lead separation for conventional lead glass when measured at room temperature.

A continuation of the baking following the attainment of the straw colored silver oxide surface would eliminate the excess caesium and increase the resistance between the electrodes and give a somewhat more sensitive antimony treated cathode, but it would ruin the oxidized silver cathode. A deficiency of caesium necessitates a longer baking at a given temperature within the above range or a higher baking temperature for an equivalent or shorter length of time. However, with such deficiency of caesium and excess baking the antimony surface becomes dark or pink-tinted with resultant low sensitivity. Consequently, I adjust the quantity of caesium liberated within the envelope to an amount within

the 1 to 3 milligrams per milligram of antimony which, within the preferred range of 2 to 3 milligrams, is a very slight excess. Under these conditions I prefer to discontinue the baking step at a time when the straw color of the oxidized silver is reached with simultaneous attainment of high antimony-caesium sensitivity. The latter sensitivity is slightly less than the maximum attainable but continued baking desensitizes the cathode 4 by continuing beyond the optimum color range. With such slight excess of caesium the baking temperature following liberation of caesium may be somewhat lower, being from 150° to 170° C., for a longer period of time such as from 6 to 30 minutes to provide the desired color range and high leakage value.

The tubulation 3 may be tipped off either before or after the liberation of caesium within the envelope although the tipping off is preferably performed after the baking operation so that any gases liberated, notwithstanding the relatively low temperature bake, may be withdrawn from the envelope. In addition, the envelope may be provided with a rarefied gas filling to obtain conventional gas sensitivity characteristics in which case following the baking step a rare gas such as argon is admitted to the envelope to a pressure of the order of 90 to 150 millimeters Hg.

While I have described my invention in accordance with the use of antimony and caesium, it will be understood that the invention is not limited to such use but that arsenic and bismuth may be substituted either in whole or in part for the antimony and that another alkali metal may be used in place of caesium. Therefore while I have indicated the preferred embodiments of my invention, it will be apparent that the invention is not limited to the exact form illustrated or to the specific method steps herein set forth and that many variations may be made therein without departing from the scope of the invention as set forth in the appended claims.

I claim:

1. A photo-tube comprising an envelope, an alkali metal-silver-silver oxide cathode and a second cathode including a coating of an alkali metal and an element selected from the group consisting of antimony, arsenic and bismuth, said first mentioned cathode having a straw color and said element a bluish color, said colors being indicative of the desired interaction of the alkali metal with the other metallic materials of said cathodes.

2. A photo-tube comprising an envelope, an alkali metal-silver-silver oxide cathode and a second cathode including a coating of an alkali metal and an element selected from the group consisting of antimony, arsenic and bismuth within said envelope, the first-mentioned cathode having a coating of silver oxide on said silver foundation of sufficient thickness to produce a straw color and said element having a bluish color, said colors being indicative of the desired interaction of the alkali metal with the other metallic materials of said cathodes.

3. The method of manufacturing a photo-tube having an alkali metal treated silver oxide foundation and a foundation including a coating of an element selected from the group of elements consisting of antimony, arsenic and bismuth comprising the steps of liberating an alkali metal within the envelope and baking the envelope until the silver oxide foundation acquires a straw color and said foundation coated with said ele-

ment acquires a bluish color devoid of a pinkish tinge.

4. The method of manufacturing a photo-tube having an alkali metal treated silver oxide foundation and a foundation including a coating of an element selected from the group of elements consisting of antimony, arsenic and bismuth comprising the steps of sealing a silver foundation and a foundation coated with said element in an envelope, oxidizing said silver foundation to a color in the range of yellow to red when viewed by reflection under white light, liberating an alkali metal within the envelope and baking the envelope until the silver oxide acquires a straw color and said foundation coated with said element acquires a bluish color.

5. The method of manufacturing a multicathode phototube comprising supporting within an envelope a cathode foundation of silver and a foundation provided with a coating of antimony, oxidizing the foundation containing said silver through a series of colors comprising the first range of colors yellow, red, blue, and discontinuing the oxidation in the second range of colors before a blackish silver oxide is produced, liberating an alkali metal within said envelope and controlling the amount of alkali metal liberated within said envelope to an amount sufficient to change the color of said silver foundation to a straw color during a final baking step, said step comprising baking said envelope within a temperature range of 150° C. to 300° C.

6. The method of manufacturing a multicathode phototube comprising supporting within an envelope a cathode foundation of silver and a foundation provided with a coating of antimony, oxidizing the foundation containing said silver through a range of colors comprising the colors yellow, red, blue, and discontinuing the oxidation in the range of the following yellow to red colors, liberating an alkali metal within said envelope and controlling the amount of alkali metal liberated within said envelope to an amount sufficient to change the color of said silver foundation to a straw color when said envelope is baked within a temperature range of 150° C. to 300° C.

7. The method of manufacturing a dual cathode phototube comprising coating a foundation with an element selected from the group of elements consisting of antimony, arsenic and bismuth to a weight corresponding to a range of 0.12 to 0.16 milligram per square centimeter, supporting within an envelope said coated foundation and a silver foundation oxidizing said silver foundation through a range of colors comprising the colors yellow, red, blue, and to a color in the range of yellow to red, liberating an alkali metal within said envelope, and baking said envelope until the oxidized silver foundation changes to a straw color.

8. The method of manufacturing a dual cathode photo-tube comprising coating a foundation with an element selected from the group of elements consisting of antimony, arsenic and bismuth to a weight corresponding to a range of 0.12 to 0.16 milligram per square centimeter, supporting within an envelope said coated foundation, a silver foundation, and an anode electrode, introducing oxygen to said envelope, oxidizing said silver foundation through a range of colors comprising the colors yellow, red, blue and to a color in the range of yellow to red, by connecting a source of positive potential to said anode electrode with respect to said silver foundation while maintaining said coated foundation floating with respect to said anode electrode and said silver foundation, liberating an alkali metal within said envelope, and baking said envelope until the oxidized silver foundation changes to a straw color.

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