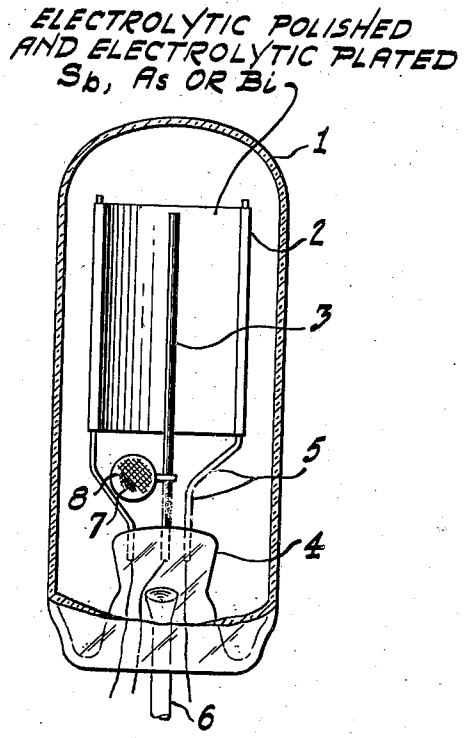
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PHOTOTUBE AND METHOD OF MANUFACTURE

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PHOTOTUBE AND METHOD OF MANUFACTURE

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My invention relates to photoelectric tubes and their method of manufacture and particularly to tubes incorporating metals of the second subgroup 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 relative high.

Copending application, Serial No. 379,010, filed by Robert B. Janes and Alan M. Glover February 15, 1941, describes a method of manufacturing phototubes incorporating metals such as antimony, arsenic and bismuth wherein the metal is deposited by vaporization and condensation upon a metal foundation, the deposited metal and foundation subjected to the atmosphere containing a minimum of water vapor followed by sealing in the utilization envelope and sensitizing with an alkali metal. In manufacturing tubes under this prior method it was found that subjecting the cathodes to high humidity atmospheric conditions, especially when at an elevated temperature, resulted in very poor sensitivity. Consequently, the excellent sensitivity obtained by my invention described below is very unexpected in view of the fact that the process inherently involves subjecting the coated cathodes to water and water vapor.

It is an object of my invention to provide a phototube having higher photosensitivity to blue light than the tubes made heretofore. It is also an object to provide a tube having exceptionally high photosensitivity to blue light and an improved 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 my invention I provide a specially prepared cathode foundation on which I deposit antimony or another equivalent metal such as arsenic or bismuth preferably by an electrolytic process. More particularly, I polish the cathode foundation to a high gloss so that its surface has a mirror-like finish. Such polishing provides a surface which under a magnification of

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about fourteen diameters is entirely free of surface scratches, cracks, crevices and sharp fissures. Furthermore, diffused reflection from such a surface is negligible and the specular reflection approaches 100 per cent.

These and other objects, features and advantages of my invention will be apparent when taken in connection with the following description thereof and the accompanying drawing wherein the single figure is a longitudinal view of a tube made in accordance with my invention.

Referring to the drawing, I 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 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 I 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 the principal teaching of my invention a metal foundation such as nickel is provided with a high glossy finish preferably by a deplating electrolytic process in a non-corrosive electrolyte which removes a portion of the foundation, leaving a smooth regular non-fissured surface. One non-corrosive electrolyte which will remove the outer layers of such a nickel foundation, leaving a brightly polished surface is a one to one solution by volume of concentrated sulphuric acid in water. With the metal foundation connected to the positive terminal of a direct current source, the surface of the foundation is removed in this solution by electrolytic action in the course of a few minutes, providing a mirror-like surface as distinguished from a mat or etched surface produced by ordinary acid etching.

In the manufacture of conventional phototubes it has long been considered, and particularly in the case of silver-silver-oxide-alkali metal phototubes it is an observed fact, that roughening or acid etching of the cathode foundation produces higher photosensitivity than with an untreated

or smooth surface. In accordance with my invention, however, I have found the direct opposite to be true where the foundations are coated with a metal selected from the second sub-group of the fifth group of the periodic system.

While I do not wish to be limited to any particular theory explaining the improved sensitivity using cathodes made in accordance with my invention, it appears that removal of the metal from the surface of the foundation in the polishing bath probably leaves a surface that is free of oxides and all contaminations and leaves no recesses on the foundation surface which may catch and retain contaminating elements. Furthermore, there may remain after the bath polishing a crystalline structure highly conducive to electron interchange or flow between the foundation and the subsequently applied coating of antimony, arsenic or bismuth. In addition, the coating does not peel from the foundation and apparently has a higher bond thereto than when applied to a non-polished surface.

As an example of one preferred method of preparing the metal foundation, I provide the cathode foundation as shown in the drawing preferably formed to whatever ultimate shape is desired and assembled with the side rods or supports 5. I then immerse the cathodes in a deplating solution, connect the foundation as an anode to the positive terminal of a direct current source and deplate at a currency density of from one to five amperes per square inch of foundation surface exposed to the solution for from two to five minutes or until the surface of the foundation acquires a highly specular mirror-like finish. Preferably, a number of foundations are simultaneously deplated, the current density being maintained with respect to the total area exposed to the deplating solution. Following the deplating operation, I immediately wash the foundations with distilled water, allowing them to remain wet or, depending upon the following treatment, I thoroughly rinse the cathodes in methanol followed by drying.

Another deplating solution or electrolyte with which particularly good results may be obtained comprises a low water content solution of fifty to ninety percent phosphoric acid by volume, the remainder being sulphuric acid, the water content being approximately 15% by weight of the volume of phosphoric acid. The deplating in this solution may be as previously indicated at a current density of about five amperes per square inch of foundation surface for a period of about two minutes. However, since in electrochemical reactions the amount of deposition or removal of metal at an electrode is a function both of time and current density, these two factors may be varied at will. The foundations are then washed in water preferably containing a wetting agent such as sulphonated alcohol known commercially as "Duponol," followed by immersion in water or by rinsing in methanol and drying in the event that the alternate process of coating the foundation with antimony or other metal as described below is followed.

The cathode foundation following the electrolytic polishing has a bright specular finish and when optically magnified at 14 diameters there is a total absence of sharply defined scratches and crevices whereas a mechanically rolled or acid-etched nickel foundation has a mat surface. There may of course be other solutions that will produce the same degree of high polish as well as

mechanical methods such as rouge or very fine abrasives for producing the high finish.

I prefer, and have obtained the best results in practicing my invention, to provide the antimony or other metal coating on the specularly polished foundation by an electrolytic process wherein the foundation, or preferably a plurality of foundations, are electroplated simultaneously either in an aqueous solution or in a solution wherein the solvent is of the organic type such as acetone, preferably utilizing as a solute the chloride of the metal to be deposited. Such a process is disclosed by Glover and Janes in their copending application, Serial No. 471,050, filed concurrently herewith.

More particularly, the preferred coating process comprises electroplating the antimony upon the foundation in an acidified solution containing antimonytrichloride. This solution may be either aqueous or of the organic type such as the following:

Aqueous solution:	
$SbCl_3$	100 g./liter
HCl (conc.)	In excess to dissolve the water insoluble white oxychlorides
Duponol	.25 g./liter
Organic solution:	
$SbCl_3$	100 g./ liter
HCl (conc.)	17 cc./liter
Duponol	.25 g./liter

The aqueous solution is maintained strongly acid to dissolve any oxychlorides which may be formed during the electrolysis, and preferably the solution contains a small amount of the wetting agent such as Duponol.

When utilizing the aqueous plating solution the foundations while still wet with water following the electrolytic polishing operation are immersed in the electrolyte, connected to the negative terminal of a direct current source and plated at a low current density such as between 0.01 and 0.05 ampere per square centimeter of exposed foundation surface. For a cathode such as utilized in the RCA 929 phototube and measuring 5/8" by 7/8" the plating energy may vary from 1 to 4 coulombs per foundation which, using an electrochemical equivalent of antimony of 0.415 milligram per coulomb, corresponds to from 0.07 to 0.22 milligram of antimony per square centimeter of cathode surface.

The maximum time the foundations are immersed in the plating solution is not critical so that the minimum rate of plating may be very low although the maximum rate of deposition is limited by the non-uniformity of plating at high current densities. The maximum current density is preferably not greater than 0.05 ampere per square centimeter of exposed foundation surface. More rapid plating produces a spotty surface, and upon final sensitization the sensitivity may be lower than optimum.

Following the plating operation the plated foundations are removed from the plating solution immediately and are immediately rinsed either with distilled water in the case of an aqueous solution or with acetone or methanol in the case of an organic solution, followed by immediate rinsing with methanol. If the rinsing operations are performed immediately after the plating operation, the cathode surfaces are of uniform color and without stain marks, whereas any intermediate drying of the foundations produces a discoloration and consequent poor

sensitivity. The foundations at this point appear grayish with a slight blueish cast and still have a very smooth surface which is specularly reflective. Following the rinsing, the foundations are immediately dried preferably in air at a temperature not exceeding 105° C. Natural drying at room temperature is preferred inasmuch as actual tests indicate that somewhat poorer results are obtained by oven drying at 105° C. for periods in excess of five minutes. If this temperature is exceeded, the grayish color with a slight blueish cast is changed and the foundations appear somewhat pinkish, this condition produced at this point not favoring high sensitivity on final processing.

During the initial manufacture of phototubes wherein the foundation was coated with antimony prior to sealing in its utilization envelope it was not expected that high sensitivity could be obtained due to the presence of water and water vapor to which the cathodes were subjected during the plating operation whether the solution was aqueous or of an organic character. Thus, even the water present in an organic solution was expected in view of prior results disclosed in the said Janes and Glover copending application to produce cathodes of very low sensitivity. Very unexpectedly, however, the process of my present invention produces high sensitivity cathodes, although care must be taken to minimize the time the wet foundations are exposed to the atmosphere and, in addition, the foundations following drying must not be subjected to an atmosphere having high water vapor content especially at elevated temperatures such as encountered during sealing of the cathodes within the utilization envelopes. Consequently, I prefer to maintain a humidity of less than 80% at 25° C. which corresponds to a desired humidity below 8 grains of water vapor per cubic foot of air, particularly during the sealing of the cathode foundation in the utilization envelope. The satisfactory results obtained are believed to be due to the fact that antimony does not oxidize when subjected to normal atmospheric conditions as it has been impossible to find any trace of antimony oxide on the antimony film following such treatment.

The antimony, arsenic or bismuth may be deposited by alternative methods, for example such as that disclosed by Janes and Glover in their copending application, Serial No. 379,010, filed February 15, 1941. Reference to that application is made for an explanation of the method and it need not be explained herein.

Following the deposition of antimony film either by the preferred or alternate processes described above 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 or activating cycles 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 preferably a small portion of the antimonoy film is vaporized to provide a clean antimony surface. The baking step both with respect to temperature and time may be controlled to produce a very slight vaporization of a portion of antimony, the baking being continued until a particular color is obtained, this color being a very light pink. This color change from a steel gray on the specularly polished foundation 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. 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° C. 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 over the tubes after it has reached the indicated temperature 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. 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.

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 the temperature of the envelope and electrode structure is maintained at such a temperature as to cause an alloying of the alkali metal with the antimony film. 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 the bulb 1 may be sealed off 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.

My invention is of particular merit in the manufacture of phototubes of the secondary emission type such as that known commercially as the RCA 931 photo-electric multiplier. The dynodes as well as the cathode of such a tube may be electrolytically coated with the antimony, arsenic or bismuth in the same manner as disclosed above except that the thickness of the coating on the dynodes is preferably from one and one-half to three times the thickness of the coating as described above of the cathode. Such difference in thickness provides a greater ratio of alkali metal to the antimony, arsenic or bismuth coating for the cathode than for the dynodes as described in Janes' copending application, Serial No. 360,255, filed October 8, 1940.

While I have described my invention in connection with the use of antimony, it is to be un-

derstood that I do not wish to be limited to this particular metal, since I have found arsenic and bismuth to be satisfactory as an equivalent of antimony. Therefore, while I have indicated the preferred embodiments of my invention of which I am now aware and have also indicated only certain specific applications for which my invention may be employed, it will be apparent that my 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 thereof as set forth in the appended claims.

I claim:

1. The method of manufacturing a light sensitive electrode comprising immersing a metal foundation in a non-corrosive electrolytic bath, deplating a portion of the metal foundation under a current density which will provide a highly specular surface on said foundation, coating the specular surface of said foundation with a metal selected from the group consisting of antimony, arsenic and bismuth, and sensitizing said coating with an alkali metal.

2. The method of manufacturing a light sensitive electrode comprising electrolytically polishing a metal foundation, electrolytically depositing antimony on said foundation to a weight between 0.07 and 0.22 milligram per square centimeter of coated foundation surface and sensitizing said coating with an alkali metal.

3. The method of manufacturing an electron emissive cathode comprising electrolytically polishing a nickel cathode foundation, electrolytically depositing antimony on said foundation, while immersed in a plating solution containing a salt of antimony, at an electrolytic current density not exceeding 0.05 ampere per square centimeter of foundation surface being plated, removing said foundation from said solution and immediately rinsing and drying said foundation, and sensitizing the deposited antimony with an alkali metal.

4. The method of manufacturing a light sensitive cathode comprising polishing in an electrolytic solution a cathode foundation to a high mirror-like finish as contrasted with a mat rolled finish, removing said foundation from said solution and while still wet immersing said foundation in an electrolytic solution containing an antimony salt as a solute, electrolytically plating antimony on said foundation to a thickness corresponding to a weight of antimony between 0.07 and 0.22 milligram per square centimeter, removing said foundation from said electrolytic solution and immediately rinsing said foundation and drying said foundation at a temperature not exceeding 105° C., sealing said foundation in a utilization envelope, evacuating said envelope and sensitizing said antimony with an alkali metal.

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