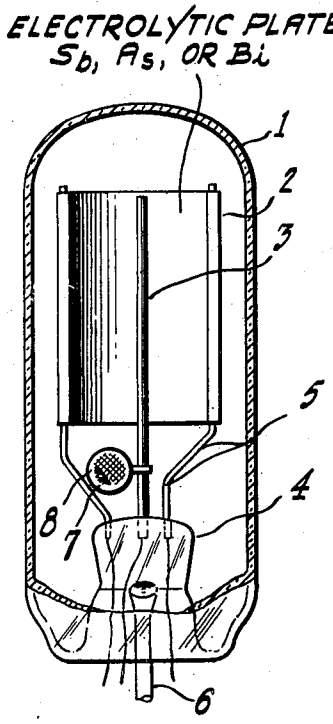
May 18, 1948. A. M. GLOVER ET AL 2,441,810

PHOTOTUBE AND METHOD OF MANUFACTURE

Filed Jan. 1, 1943



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Patented May 18, 1948 2,441,810

UNITED STATES PATENT OFFICE

2,441,810

PHOTOTUBE AND METHOD OF MANUFACTURE

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Application January 1, 1943, Serial No. 471,050

11 Claims. (Cl. 316—18)

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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.

In our copending application, Serial No. 379,010, filed February 15, 1941, and now Patent No. 2,401,735, issued June 11, 1946, we described a method of manufacturing phototubes incorporating metals such as antimony, arsensic and bismuth wherein the metal was deposited by vaporization and condensation upon a metal foundation surface, 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 our 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 our 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 our 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 our invention we provide a cathode foundation on which we deposit anti-

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mony or another metal of the second sub-group of the fifth group of the periodic system at a predetermined rate by an electrolytic plating method 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 preferably 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 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 the single figure is a longitudinal view of a tube made in accordance with our invention and incorporating a cathode comprising an alkali metal sensitized film of metal deposited by our novel process.

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, which is made of nickel or other base metal, is preferably supported by a stem or press 4 preferably of lead glass 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 electrolytically deposited on a cathode foundation 2 of nickel or other base metal prior to sealing the cathode foundation with the bulb 1 and so deposited that the antimony film is applied by electrolytic displacement of the metal from a salt solution.

We have found that when depositing antimony by electrolysis on a foundation, it is desirable to limit the time during which the antimony is exposed to the solvent, particularly when it is simultaneously exposed to the atmosphere, 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 either at a high rate or when exposed to the atmosphere while wet for too great a period of time have resulted in tubes of poor sensitivity. Furthermore, deposition of the antimony either in an aqueous or nonaqueous solution must not be at too great a rate, inasmuch as we have found that lower sensitivity is obtained when the antimony is deposited at too high a rate.

The antimony employed as an anode in the electrolytic process 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 500 to 1500 angstroms may be sensitized to obtain high photosensitivity when illuminated by light from a tungsten light source operating at 2870° K.

As an example of one preferred method of depositing the antimony or the equivalents, namely, arsenic and bismuth, a plurality of metal foundations may be coated simultaneously either in an aqueous solution or in a solution wherein the solvent is of the organic type such as acetone, preferably utilizing the chloride of the metal to be deposited as a solute. In addition, when using an aqueous solution we prefer that it be acidified to dissolve any oxychlorides which may be formed during the electrolysis. Furthermore, we prefer to provide in the solution a small amount of a wetting agent such as sulphonated alcohol, sold under the trade name of "Duponol." Prior to the plating process the cathode foundations are thoroughly cleaned and we have found the electrolytic polishing method of cleaning and preparing the foundation as described by John B. Diffenderfer in his application, Serial No. 471,049, filed concurrently herewith, and now Patent Number 2,401,738, issued June 11, 1946, to be a preferred method of cleaning and foundation preparation. In substance, this process comprises a deplating operation of the nickel or other metal foundation by connecting the foundations as anodes in an aqueous solution of sulphuric acid maintained at room temperature or below. Preferably, the solution is made in a ratio of 1 to 1 concentrated sulphuric acid in water by volume. The foundations are then deplated at a current density of from 1 to 5 amperes per square inch for from 2 to 5 minutes or until the surface of the foundation acquires a highly mirror-like finish. Following this cleaning, the foundations are immediately rinsed in distilled water and immediately placed while wet in our antimony plating solution. We have found the following solutions to be admirably suited for providing the proper conditions under which the foundations are coated with antimony, although the quantities

indicated my be varied over wide limits without materially affecting the deposition of the antimony.

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

We have found that the amount of antimony deposited on the foundation is relatively critical and that preferably the amount deposited by electrolysis should correspond to a calculated weight of 0.07 to 0.22 milligram per square centimeter of active cathode surface. Inasmuch as the cathode foundations are immersed in the plating solution and plated with the antimony as cathodes utilizing an antimony anode, the deposit is over the entire surface exposed to the solution. Consequently, the current in passing through the solution as well as the time must be controlled in accordance with the total exposed foundation surface. More particularly, we have found that a quantity of antimony corresponding to deposition under 0.14 to 0.57 coulomb per cm^2 provides the best cathodes, although this factor may likewise be varied but with somewhat poorer sensitivity upon final sensitization.

The metal foundations may be formed to the arcuate shape shown in the drawing and assembled with the side rods 5 prior to the cleaning operation, whereupon following cleaning, the side rods serve as connectors in the electrolytic plating circuit. For a cathode such as utilized in the RCA 929 phototube and measuring 5/8" by 7/8" the plating energy may vary from 1.0 to 4.0 coulombs per foundation which, using an electrochemical equivalent of antimony of .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 coated foundations 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 or other organic washing agent. 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 result in poor sensitivity. The foundations at this point appear grayish with a slight blueish cast. Following the rinsing, the foundations are immediately dried, preferably in dry 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. If this temper-

ature is exceeded, the grayish color with a slight blueish cast is changed and the foundations appear somewhat pinkish, this condition occurring prior to exhaust not favoring high sensitivity on final processing.

During the construction of the first phototubes made in accordance with our invention 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 our prior results disclosed in our said copending application, to produce cathodes of very low sensitivity. Very unexpectedly, however, the process of our present invention produces high sensitivity cathodes, although care must be taken to minimize the time the foundations are simultaneously exposed to the solution and 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, we 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 during the time the plated foundations are exposed to the air and particularly when they are heated above room temperature, such as during the sealing within the utilization envelopes. The satisfactory results which we have 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. While we do not fully understand the action of humidity in producing unsatisfactory results, this may be due to the formation of an exceedingly thin film of antimony oxide on the underlying antimony. Following the plating of the antimony film and after drying, the prepared foundations are sealed into individual envelopes and the envelopes exhausted. Preferably, the sealing operation is performed in an air-conditioned room so that the humidity may be maintained at a low value. During actual manufacture of tubes having antimony coated cathode foundations in the summer months and under regular factory conditions the percentage of tubes having low sensitivity was quite high, often running to 80%, whereas during the same operations performed under low humidity conditions with air-conditioning facilities the loss of tubes was practically negligible from this factor of high humidity. No oxygen, whatsoever, is introduced within the tube during the exhaust cycle or sensitizing operations and in fact such introduction of oxygen substantially destroys the sensitivity of the completed tube. The tube is then baked to remove occluded gases and in accordance with our prior invention referred to above a small portion of the antimony film may be vaporized to provide a clean antimony surface. Thus, 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 cathode color is obtained, this color being a very light pink. This color change is from a steel gray to a just perceptible pinkish color and 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.

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. 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 nonexistent 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 a plated antimony film thickness or coating weight having rather narrow limits. 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 when sensitizing a cathode of the above

dimensions coated on both sides with the use of a pellet 7 weighing 40 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 photo-cathode. 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.

Our 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 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. Inasmuch as a single tube of the RCA 931 type has nine dynodes, the coating process time is greatly reduced over older methods with greater uniformity and high secondary electron emissivity by following our method.

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 photo electric tube which comprises electrolytically depositing a film of metal selected from the group consisting of antimony, arsenic and bismuth on an electrically conductive foundation, sealing said foundation in an envelope, evacuating said envelope and subjecting said coated foundation to the vapor of an alkali metal.

2. The method of manufacturing a photo electric tube comprising electrolytically plating on a metal foundation a film of metal selected from the group consisting of antimony, arsenic and bismuth at a current density not exceeding 0.05 ampere per square centimeter of exposed foundation area, sealing said foundation in an envelope, evacuating said envelope and sensitizing said coated foundation with an alkali metal.

3. The method of manufacturing a photo electric tube comprising immersing a metal foundation in a solution containing a solute of an antimony compound, electrolytically plating antimony on said foundation at a current density not exceeding 0.05 ampere per square centimeter of exposed foundation area, drying said foundation, sealing said foundation in an envelope and sensitizing said plated foundation with an alkali metal.

4. The method of manufacturing a photo electric tube comprising immersing a metal foundation in an organic solution containing an antimony compound and an immersed antimony electrode, electroplating antimony on said foundation, removing said plated foundation from said solution, rinsing said foundation with an organic washing medium, drying said foundation, sealing said foundation in an envelope and photosensitizing said foundation with an alkali metal.

5. The method of manufacturing a photoelectric tube comprising immersing a metal foundation in an aqueous solution containing an antimony compound, electroplating antimony to a weight corresponding to from 0.14 to 0.57 coulomb per square centimeter on an exposed surface of said foundation, removing said foundation from said aqueous solution and immediately rinsing said foundation in a nonaqueous medium, drying said foundation, sealing said foundation in an envelope and sensitizing said foundation with an alkali metal.

6. The method of manufacturing a photoelectric tube which comprises electrolytically depositing a film of a metal selected from the group consisting of antimony, arsenic and bismuth on an electrically conductive foundation having an extended area, subjecting said foundation and said film to the atmosphere, sealing said foundation bearing said film in an envelope, evacuating said envelope to provide a nonoxidizing atmosphere within said envelope, heating said foundation and film at an elevated temperature, and depositing an alkali metal on said film to render said film electron emissive.

7. The method of manufacturing a photoelectric tube which comprises supporting an electrically conductive foundation having an extended area in an electrolytic bath containing a salt of a metal selected from the group consisting of antimony, arsenic and bismuth, electrolytically depositing a film of said metal on said foundation with 0.14 to 0.57 coulomb per square centimeter, drying said foundation and said film, sealing said foundation bearing said film in an envelope, evacuating said envelope to provide a nonoxidizing atmosphere within said envelope, baking said envelope at a temperature between 275° C. and 325° C., and depositing an alkali metal on said film to photosensitize said film.

8. The method of manufacturing a photoelec-

tric tube which comprises depositing a film of antimony on an electrically conductive foundation in an aqueous acidified electrolytic solution having an antimony salt as the solute, removing the solution from said antimony film, immediately drying said film, sealing said foundation bearing said film in an envelope, evacuating said envelope to provide a nonoxidizing atmosphere within said envelope, depositing an alkali metal on said film and baking said film to photosensitize said film.

9. The method of manufacturing a photosensitive electrode which comprises supporting a metal foundation in an electrolytic bath containing an antimony salt, electrolytically depositing a film of antimony on said foundation until the thickness of said film is equivalent to a weight of 0.07 to 0.22 milligram per square centimeter area of said foundation, baking said film in a nonoxidizing atmosphere, depositing an alkali metal on said film, and baking said film to photosensitize said film.

10. The method of manufacturing photosensitive devices which comprises supporting a plurality of metallic members in an electrolytic solution having a salt of antimony as a solute, electrolytically forming a film of antimony on each of said members, removing the members from said solution, immediately washing and drying each of said members, sealing said members within a space to be evacuated, evacuating said space and subjecting the metallic members to the vapor of an alkali metal to photosensitize the film of antimony.

11. The method of manufacturing photosensitive devices which comprises supporting a plu-

rality of metallic members in an organic solution of an antimony salt, electrolytically forming a film of antimony of a thickness corresponding to a weight of 0.07 to 0.22 milligram per square centimeter on each of said members, removing the members from said solution, washing and drying each of said members before normal atmospheric drying of said members occurs, sealing said members in a space to be evacuated, evacuating said space, baking said members until the said films assume a pinkish color, and subjecting the metallic members to the vapor of an alkali metal to photosensitize the film of antimony.

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