April 20, 1937. A. J. McMASTER ET AL 2,077,633

PHOTOELECTRIC TUBE

Filed June 14, 1930

Fig. 1.

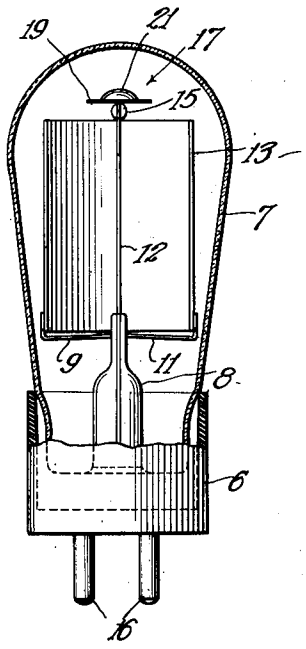


Fig. 2.

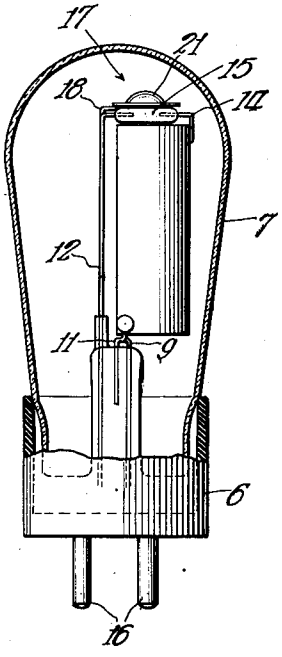
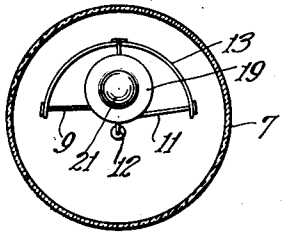


Fig. 3.



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PHOTOELECTRIC TUBE

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15 Claims. (Cl. 250—27.5)

Our invention relates to photo-electric tube and to a method for making such tube.

A photo-electric tube in order to meet the requirements of present day commercial use, should be sensitive over the entire visible spectrum of light, and particularly in the region of yellow and red light, since the incandescent lamp commonly used in association therewith is a strong emitter of light of this order. In many cases it is desirable to provide photo-electric tubes which have a maximum sensitivity for particular colors or wave lengths of light. We have discovered a method of pre-determining the maximum sensitivity of photo-electric tubes for specific colors.

An object of the invention is to provide a new and improved photo-electric tube and method of making the same.

A further object is to provide a photo-electric tube and method of making the tube having high sensitivity for all colors of light in the visible spectrum.

A further object is to provide a tube having high sensitivity in the red and yellow region of the light spectrum.

A further object is to provide a new and improved light sensitive surface, and a method of preparing such a surface.

A further object is to provide a new and improved method for scavenging a photo-electric tube.

Other objects and advantages will appear as the description proceeds.

It has been found that there are a large number of factors affecting the final characteristics of a photo-electric tube, each of which must be taken into careful consideration to obtain uniformly good results. In order to eliminate the haphazard construction of photo-electric tubes, and the selecting of a few tubes which have the proper characteristics, we have made elaborate experiments to determine the exact conditions necessary for obtaining uniformly good results. It has been found that the electron emitting surface of a photo-electric tube should be extremely thin. However, a thin photo-electric surface has a low conductivity and it is difficult to make good electrical contact therewith, and therefore, we provide a conducting base such as copper, silver, magnesium, gold, or other low resistance metals underneath the photo-electric surface.

A complete understanding of the invention may be had by reference to the following description taken in conjunction with the accompanying drawing, in which

Fig. 1 is a side elevation of a tube embodying the invention, and made in accordance with the method of the invention,

Fig. 2 is a similar elevation in which the tube is rotated through an angle of 90 degrees from that shown in Fig. 1, and,

Fig. 3 is a plan view of the tube.

In practicing the invention a base 6 is provided having an envelope 7 mounted thereon, and within the envelope is a stem or press 8, having a pair of supports 9 and 11 mounted thereon. Forwardly of these supports is a further support 12 which also serves as the anode of the tube. Supports 9 and 11 carry a semi-cylindrical plate 13 which is processed to provide a light sensitive surface. In order to prevent microphonic noises due to relative movement between the anode 12 and cathode 13, the upper portion of cathode 13 is provided with a support 14 which is mechanically connected with the upper end of anode 12 by means of an insulating insert 15, preferably of glass or porcelain, which holds the cathode and anode in fixed relative positions. Electrical contact is made with the anode and cathode through prongs 16, one of which is connected to the anode, while another is connected to the cathode. While the plate 13 may be made of the materials enumerated above, it is preferably made by silver-plating a copper plate. Extreme precautions must be taken in electro-plating with silver on the copper plate in order to avoid the production of materials as the result of chemical reactions, which will deleteriously affect the light sensitive surface which is later applied thereto.

We have found that the following method of electro-plating avoids the presence of undesirable ingredients in the finished plate.

A copper plate is first immersed in sodium hydroxide, after which it is boiled in clear water. The plate is then immersed in a dilute solution of nitric acid. This etching process produces a crystalline surface of a somewhat rough appearance. This rough structure produced thereby is highly desirable later in the oxidation of the plate, since the rough surface presents a greater area and oxidizes more readily and thoroughly than a smooth surface. The copper plate is then washed in the water and dipped in sodium cyanide.

When the plate is removed from the cyanide solution it is immediately electro-plated, before allowing it to dry, since if it is left to dry it tends to leave uneven spots on the plate. Because of the rough character of the copper surface on which the silver is plated, this silver layer also exhibits a certain roughness on its sur-

face. The electro-plated plate is then mounted on the stem in the envelope 7 together with the anode as described above.

Simultaneously with the mounting of the elements in the envelope, a capsule or pellet 17 is mounted in the upper portion of the envelope on a support 18 which is secured to the upper end of the anode by welding or the like. The pellet consists of a disc 19 having a bead 21 of an alkali or alkaline earth metal salt mixed with calcium or some other element having a higher affinity for the radical or element of the salt than the alkali or alkaline earth metal, from which the alkali or alkaline earth metal is evaporated and deposited upon the cathode. If for instance we wish to make a caesium tube the pellet may consist of a mixture of caesium chloride and calcium. This mixture, upon heating the pellet, forms calcium chloride and liberates caesium. The particular alkali or alkaline earth metal salt used depends upon the characteristics desired in the tube. If we wish to obtain a tube which is highly sensitive to light in the red and yellow regions of the spectrum we use a caesium salt such as caesium chloride, caesium carbonate, caesium nitrate, caesium trinitride, caesium silicate, caesium dichromate, or caesium azide. If we wish to obtain a tube responsive to shorter wave lengths we use potassium chloride, potassium carbonate, potassium nitrate, potassium trinitride, potassium silicate, or potassium azide. For still shorter wave lengths salts of the alkaline earth metals are used such as barium, strontium, and magnesium carbonates. All of these metals are high in the electromotive series. The method of processing the silver plated copper plate in the tube will first be described in connection with the caesium salts.

After the elements and the pellet of caesium salt have been mounted in the envelope, the envelope is placed on an evacuating pump and exhausted. At the same time the envelope or bulb is placed in an oven to heat the bulb and expel the gases therefrom, and also to preliminarily expel the gases from the elements within the bulb. The cathode is then inductively heated by means of a high frequency current coil which is associated therewith in such a manner that the major portion of the lines of flux link with the portion of the plate adjacent the stem in order to avoid overheating of the disc 19 supporting the pellet. After the bulb and elements have been thoroughly heated and exhausted to remove the gases from the tube, the envelope and elements are allowed to cool while the evacuation is maintained.

When the elements and bulb have been sufficiently cooled, about one to two millimeters of oxygen is admitted into the bulb and a glow discharge is produced between the anode and cathode with the cathode as the negative electrode, for about two minutes or less. The proper time can be readily determined by experiment from the color changes of the cathode. The glow discharge causes a chemical reaction between the silver surface on the cathode and the oxygen and converts the silver on the cathode to a silver oxide. On account of the roughened surface of the silver plate obtained as pointed out above, the oxidation is enhanced and covers a larger area than would be the case upon a perfectly smooth surface. The cathode being thoroughly oxidized, the bulb is again evacuated and metallic caesium is evaporated from the pellet by inductively heating disc 19. It will be noted that the disc is at right angles to the axis of the cathode, and therefore the pellet may be heated without causing much heating of the cathode, and the cathode being cooler than the disc, the metallic caesium tends to deposit upon the cathode. In order to prevent the caesium from being deposited on the inner walls of the bulb, the bulb is heated during this operation in an oven to a temperature of from 150° to 170° C. During this step evacuation is maintained and the bulb remains considerably hotter than the cathode. The heating of the bulb is continued until no excess caesium is left in the tube. However, care must be taken not to apply too high a temperature to the bulb since that would overheat the cathode, and thus again liberate the caesium which has been deposited on the cathode. In this step the caesium is deposited in a thin film on the silver oxide and some of the caesium combines with oxygen liberated by the silver oxide. It was stated that the heating and evacuation are continued until no excess caesium is left in the bulb. Some of the caesium appears to be absorbed by the caesium oxide and the best results are obtained when the layer of metallic caesium thereon is as thin as possible. It appears that the light sensitive characteristics of the cathode are probably due to metallic caesium, and the caesium absorbed by the underlying caesium oxide seems to replace the caesium which leaves the cathode. The metallic caesium appears to be present as a thin adsorbed film on the surface of the cathode and this film serves as the light sensitive electron emissive agent.

It has been found that by making the stem 8 of the bulb of lead glass some of the excess caesium reacts with the lead glass stem as shown by a brownish discoloration of the stem and aids in cleaning up or scavenging the tube. The envelope is, however, made of lime glass since discoloration of the envelope would decrease its transparency.

The bulb may now be sealed off, and is ready for use. However, in most cases it is found desirable to admit an inert gas such as argon, helium, neon, krypton, xenon, or even a less inert gas such as nitrogen, before the bulb is sealed off. Such gases increase the sensitivity of the tube due to partial ionization when an electron current flows in the tube as is well known in the art. If it is found, upon testing the tube, that it does not have the expected sensitivity, the sensitivity may be increased by passing a glow discharge through the inert gas. By making the cathode positive it may be bombarded by electrons to increase the concentration of the light sensitive metal on the surface of the cathode, and by making the cathode negative, the concentration of the metal on the surface of the cathode may be decreased. By this method the requisite concentration of the light sensitive metal for maximum sensitivity is obtained and substantially uniform and predetermined results are obtained, which eliminates the waste and shrinkage found in following methods heretofore used.

The process may be carried out in a similar manner in using potassium to obtain a cathode having maximum sensitivity for shorter wavelengths of light by employing pellets of a potassium salt, or when it is desired to use alkaline earth metals instead of caesium, to provide a cathode having maximum sensitivity for still shorter wave-lengths of light the pellets are formed of alkaline earth metal salts as pointed out above.

An alternative method may be used with potassium or caesium. Instead of electro-plating silver upon a copper plate, the copper plate may be directly oxidized and the potassium or caesium deposited upon the copper oxide surface in forming the light sensitive surface.

It will be understood that the nature and embodiments of the invention herein described and disclosed are merely illustrative and that many changes and modifications may be made therein without departing from the spirit and scope of the invention.

What we claim as new and desire to secure by United States Letters Patent is:—

1. A method of making a photoelectric tube which consists of electroplating a copper plate with silver and producing a rough silver surface, mounting the plate and an anode in an envelope, expelling gases from the envelope and elements, admitting oxygen into the envelope, oxidizing said silver surface, depositing metallic caesium on the oxidized surface and removing excess caesium from the tube.

2. A method of making a photoelectric surface which consists of cleansing a copper plate, immersing the plate in nitric acid thereby roughening the surface, electroplating the plate with silver, oxidizing the silver plate and depositing a metal high in the electromotive series thereon.

3. A method of preparing a photoelectric surface which consists of immersing a copper plate in sodium hydroxide, washing the plate in water, immersing the plate in nitric acid, rinsing the plate in water, immersing the plate in sodium cyanide, electroplating the plate with silver before drying, expelling occluded gases from the plate, oxidizing the plate, depositing an alkali metal upon the oxidized plate, and removing the excess of said metal from the plate.

4. A method of making a photoelectric tube which consists of mounting a plate having a silver surface and an anode in an envelope, supporting a pellet of a salt of an alkali metal and a metal having an affinity for the negative radical of the salt when heated in the envelope, oxidizing the silver surface in the envelope by producing a unidirectional glow discharge to pass electrons from the plate to the anode in the presence of oxygen, removing the excess oxygen from the envelope, heating said pellet to evaporate the alkali metal and deposit it upon the plate, and removing the excess of the alkali metal.

5. A method of making a photoelectric tube which consists of mounting a silver surface cathode plate and an anode in an envelope, supporting a pellet of a salt of an alkali metal in the envelope, oxidizing said silver surface, and heating said pellet to evaporate the alkali metal, maintaining the envelope hotter than the plate to deposit said evaporated metal on the plate and removing the excess of the alkali metal leaving a thin adsorbed film upon the plate.

6. A method of making a photoelectric tube which consists of mounting a silver surface cathode plate and an anode in an envelope, expelling gases from the envelope and elements, oxidizing the silver surface, depositing an alkali metal film on the silver oxide, removing the excess of said metal from the tube, admitting an inert gas, and producing a glow discharge between the cathode and anode to obtain the requisite concentration of the alkali metal film on the cathode.

7. A method of making a photoelectric tube which consists of providing an oxide coated cathode and an anode in an envelope, depositing an alkali metal film on the oxide coating, expelling the excess alkali metal, admitting an inert gas into the envelope and producing a glow discharge with either the cathode or anode negative depending upon the concentration of the film of alkali metal on the cathode.

8. A method of making a photoelectric tube which consists of mounting a silver surface cathode and an anode in an envelope, supporting a pellet of an alkali salt therein, heating the envelope in an oven to expel gases therefrom, inductively heating the cathode to expel gases therefrom, exhausting said gases, allowing the tube to cool, admitting oxygen to the tube, producing a glow discharge to oxidize the silver surface, removing the free oxygen from the envelope, inductively heating the pellet to chemically release and evaporate the alkali metal and deposit it on the cathode, and removing the excess alkali metal from the envelope.

9. A method of producing a light responsive, electron emissive surface which comprises the following steps, etching a metallic surface, electroplating a metal on said surface, oxidizing the surface of the plated metal and depositing an alkali metal on the oxidized surface.

10. The method of producing a light responsive, electron emissive surface which comprises the following steps, etching a metallic surface, oxidizing said surface and depositing an alkali metal thereon.

11. The method of producing a light responsive, electron emissive surface which comprises the following steps: roughening a metallic surface, depositing a metallic layer thereon, oxidizing the surface of said layer and depositing an alkali metal on the oxidized surface of said layer.

12. A photoelectric tube comprising an envelope, and an anode and a cathode therein, said cathode comprising a metal base portion other than silver, a rough surfaced layer of silver thereon, a layer of silver oxide over said silver and an alkali metal deposited on said silver oxide.

13. A photoelectric tube comprising an anode, a cathode other than silver, the cathode having a roughened surface, a rough surfaced coating of electroplated silver on said rough surfaced cathode, a silver oxide coating on said silver coating, said silver oxide coating having an alkali oxide intermingled therewith, and a thin film of an alkali metal upon said silver oxide coating.

14. A method of preparing a photoelectric surface which comprises the following steps: cleansing a metal surface, etching the surface, coating the surface with silver, oxidizing the resulting silver surface and depositing an alkali metal thereon.

15. The method of producing a light sensitive electro-responsive device which includes immersing a metal surface in acid, removing the acid from said surface and subsequently forming a light sensitive layer on said surface.

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