March 2, 1937. A. J. McMASTER ET AL 2,072,342

PHOTOELECTRIC TUBE

Filed Sept. 2, 1930

Fig. 1

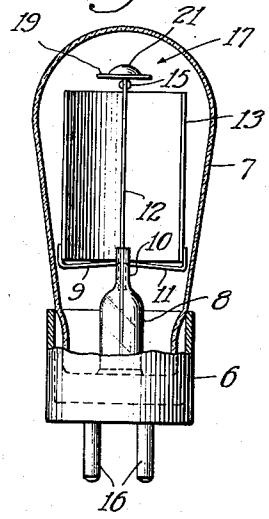
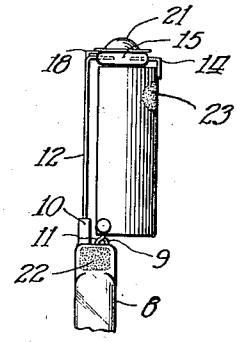


Fig. 2



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PHOTOELECTRIC TUBE

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3 Claims. (Cl. 250—27.5)

Our invention relates to photo-electric tubes and more particularly to a method and means for scavenging or cleaning up the vapors and gases in such tubes.

This application is a continuation in part of our copending application, Serial No. 461,117, filed June 14, 1930, which relates to photo-electric tubes and method of making such tubes.

In providing a cathode plate of a photo-electric tube with an electron emissive coating it is found that this coating should be as thin as possible to obtain the best results. Such a coating has been referred to as a monatomic layer. However, in practice it is impossible to uniformly deposit such a layer unless an excess of coating is first applied and the excess subsequently removed from the cathode and eliminated from the tube. The present invention is directed to a method and means for eliminating the excess vapors and gases from the tube.

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

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.

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, and

Fig. 2 is an elevation of the mount of the tube rotated through an angle of 90 degrees from that shown in Fig. 1.

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 any of the materials enumerated in the above noted copending application, it is preferably made by silver plating a copper plate. Mounted on the press 8 is a small tube or collar 10 which may be made integral with the press. This collar surrounds the base of anode 12 but is spaced therefrom leaving a small circular gap or space between the anode and collar. When the alkali metal is deposited on the elements of the tube none of the metal will be deposited in this circular space and it serves therefore to effectively prevent a short circuiting or conducting layer from being deposited between the anode and supports 9 and 11 of the cathode.

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. Preferably, the silvered plate is provided with a rough surface in the manner described in the above mentioned copending application. The roughened surface enhances oxidation and causes the same to cover 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 scavenging of the tube is extremely important in producing a high quality of tube of high sensitivity and therefore it is advisable to supplement the scavenging resulting from the use of the lead glass stem by providing a separate scavenging composition, or the separate scavenging composition may be used as an alternative. This is done by providing a metallic oxide such as lead monoxide (PbO), lead dioxide (PbO_2), lead oxide red (Pb_3O_4), or lead sesquioxide (Pb_2O_3) within the tube which readily reacts with the alkali metal and removes it from the tube. Many other metallic oxides may be used, the above list being merely illustrative.

In applying the metallic oxide to some internal parts of the tube a binding agent, causing the oxide to adhere to the part to which it is applied, may be used. An aqueous solution of soluble salts is used in small quantity and mixed with the oxide to form a thick paste. This mixture is applied to some part of the tube as for instance to the stem or press as shown at 22 or to the back of the plate as at 23. It has also been applied to an inconspicuous part of the inner wall of the bulb with good results. After the application of the mixture it is allowed to dry for several hours before the tube is assembled and evacuated.

The binding agent should be one of high melting temperature and of high decomposition temperature in order that it will not melt or decompose during the processing of the tube. The action of the binding agent, which is the soluble salt, is to form upon drying a crystal structure which binds together the colloidal or insoluble particles of the oxide which act as the scavenging agent. The chlorides of sodium or potassium, as well as many other common salts which are soluble in water, have been found to be very satisfactory as the binding agent. The heating of the mixture during the exhaustion and expulsion of the excess vapors enhances the scavenging action of the mixture.

The effect of the use of the scavenging composition is to aid in the elimination of the excess alkali metal from the tube thereby supplementing the heating and evacuation and resulting in a more perfect product.

The bulb may now be sealed off, after the scavenging process, 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 wave-lengths 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.

I claim:

1. A method of scavenging an electronic tube which consists of mixing a lead oxide with an aqueous solution of a water soluble salt, and placing the mixture in a tube to clean up alkali vapors.

2. A method of scavenging a tube which consists of forming a paste of a lead oxide and a water soluble salt, painting said paste on a part within the tube, and heating the paste to remove alkali vapors from the tube.

3. An electronic tube comprising an envelope having a plurality of electrodes mounted therein, an alkali metal in said envelope, and a paste of a mixture of a solution of a water soluble salt and an oxide of lead applied to an inside portion of the tube to remove excess alkali metal from the tube.

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