

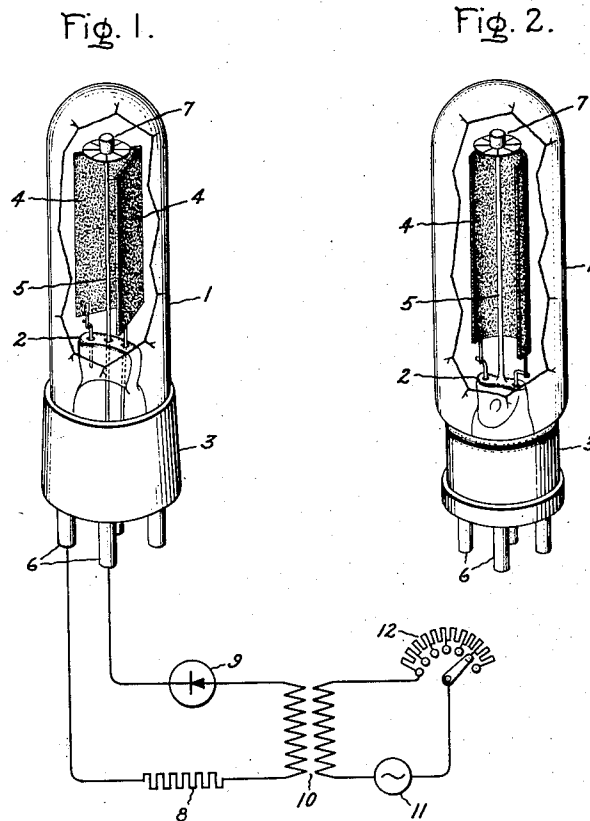
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E. E. CHARLTON

1,927,792

PHOTO-ELECTRIC TUBE

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PHOTO-ELECTRIC TUBE

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3 Claims. (Cl. 250—27.5)

The present invention relates to photo-electric devices and includes in particular a novel method of treating the light-sensitive surface. The invention is concerned more especially with that portion of the treatment which involves the oxidation of the foundation metal preparatory to receiving the light-sensitive material. The technique of manufacture improved in accordance with the present invention provides a surface which is much more sensitive to light than surfaces heretofore obtained.

In order more clearly to explain the difference between the process as improved in accordance with my invention and the usual technique, I have illustratively exemplified the improved process as applied to two types of photo-electric tubes now in common use. Fig. 1 shows a photo-electric tube having a cathode of double-plate construction while in Fig. 2, the cathode takes the form of a single semi-cylindrical member. Both of these types employ cathodes physically separate from the envelope but it is to be understood that my invention applies equally well to photo-electric tubes in which the light-sensitive surface is formed as a coating on the interior of the envelope.

Referring to Fig. 1, numeral 1 designates an evacuated envelope which may be filled with gas if desired, and terminating in a reentrant stem 2. For reasons which will appear presently, the envelope is made preferably of lime glass and the stem 2 preferably of lead glass. The bottom of the envelope is sealed in a standard base 3. The envelope contains a cathode consisting of two plate members 4 disposed at an angle to one another and coated with a light-sensitive substance in a manner described hereinafter. The cathode may be made of any suitable metal but nickel and copper are preferred since these metals lend themselves to being silver-plated, as will be explained later, and to being formed as comparatively thin but rugged plates.

The envelope also contains an anode which consists of an upright rod or wire 5, preferably of nickel, and equidistantly arranged between the plate members 4. The electrodes are supported in any suitable manner from the stem 2 and connections made to terminals 6 of which four are shown to conform to a standard radio tube socket, but only two actually are used for contact purposes.

Resting on top of the rod-like anode 5 and out of contact with the cathode, there is positioned a capsule 7 which contains a compound which evolves light-sensitive material upon being heat-

ed. The photo-electric tube shown in Fig. 2 is similar to that illustrated in Fig. 1 except that the cathode 4 takes the form of a semi-cylinder arranged concentrically with respect to the rod-like anode.

The first step after forming the cathode into the desired shape is to coat the same with silver, and this may be conveniently accomplished by immersing the copper member in an electrolytic bath containing silver or by evaporation in the well understood manner. Both sides of the copper member are coated by this process but it will be understood that only the inner side of the cathode is normally activated by light and for this reason only this side need have the silver plating. The silver-plated member may then be introduced into the envelope together with the cooperating rod electrode with the capsule attached.

The envelope is then placed on the pump, exhausted, and at the same time, an oven is lowered over the envelope and heated to approximately 350° C. for a "bake-out". When it is determined that all of the deleterious gases such as water vapor and the like have been removed from the envelope, the tube is allowed to cool to room temperature at which time the pump connection is shut off and oxygen in small doses admitted until a pressure of about 250 to 300 microns Hg is reached.

The silver-plated member 4 is then oxidized. Whereas in the prior art this oxidation step was accomplished by heating the tube in an oven to a relatively high temperature for a period depending upon the degree of oxidation required, I have found that the oxidizing step may be more accurately and conveniently accomplished by electrical methods.

In accordance with my invention, I propose to oxidize the member by immersing the latter in a glow discharge, which is readily produced by applying a relatively high voltage between the rod 5 and the member 4. The voltage may be obtained from any suitable source such as a high frequency induction spark coil or a high voltage battery, but I prefer to employ high voltage direct current obtained from a rectifying arrangement. A current produced in this manner may readily have a voltage of 1000 or more which is ordinarily sufficient to produce a glow discharge in oxygen at the pressures mentioned when the rod 5 is made the positive terminal and the member 4 the negative terminal. It will be understood that higher pressures of oxygen may be used for this purpose, for example, as high as 1 to 2 millime-

ters of mercury, in which case the voltages employed may be considerably less, for example, of the order of 300 to 500 volts. A current limiting resistance 8 preferably is connected in series with the tube, as shown in Fig. 1, as a protection against overload during the oxidation process. It is apparent that a high degree of control may be exercised over the applied voltage so that the oxidation step is carried out with extreme accuracy, i. e. as to depth of oxidation, also with considerable uniformity as between tubes manufactured on a quantity production basis. It has also been noted that by means of the electrical oxidation treatment, the depth of the oxide layer may be increased over the layers obtained by other treatments so that a larger proportion of the silver is converted into silver oxide and a corresponding increase of light-sensitive material is absorbed by this surface, as will appear hereinafter.

In the event that higher pressures of oxygen and lower voltages are employed for the oxidation treatment, the current flowing through the glow discharge may become large, in fact, so large as normally to heat the cathode to a temperature higher than the decomposition temperature of silver oxide. Consequently, it is necessary to maintain the cathode surface as cool as possible under these conditions and for this purpose, a fan or other heat radiating or dissipating device may be used to advantage. It has been observed that the presence of heat during the improved oxidation process is not at all necessary, although a certain amount of heat is not objectionable provided the temperature of the cathode is not elevated beyond decomposition temperatures.

While the manner in which the oxidation takes place is not accurately known at the present time, I believe that the phenomenon depends for its effectiveness insofar as the ultimate increase of light-sensitivity is concerned, on the fact that the silver-plated member is bombarded by oxygen ions and in addition, is immersed in an atmosphere of ozone. Regardless of the correctness of this belief, I have found as a fact that tubes containing cathodes which have been oxidized in accordance with my invention exhibit the quality of light-sensitivity to a much greater extent than tubes in which the cathode has been oxidized in other manners, such as being heat-treated in an oven.

In Fig. 1, I have shown the rectifier 9 in a generic manner, supplied with alternating current through a standard type of transformer 10, the primary of which is energized by a suitable source 11 of low voltage alternating current.

When a desired degree of oxidation has been obtained, which can be controlled conveniently and accurately by simply regulating the applied voltage, for example, by a rheostat 12 which will also constitute a current limiting resistance, and time during which the voltage is applied, the excess oxygen is pumped out and a highly light-sensitive material introduced into the envelope. This material may consist of caesium, rubidium or other reactive metal and is contained in the capsule 7, shown as mounted at the upper end of the rod anode but which may be supported at any other part of the electrode structure. Pellets of dichromate of caesium and a suitable reducing agent, such as silicon, advantageously are used for this purpose.

The capsule may be flashed by means of current introduced from a high frequency coil,

whereupon the alkali metal is released and condenses on the silver-plated member 4 as well as other portions of the electrode structure and envelope. The tube is then heated, preferably by lowering the oven, for a short time in order to revaporize the caesium which has condensed on the envelope wall and to cause the same to recondense on the silver. The length of time of the second "bake-out" depends not only upon the amount of silver oxide present on the member 4, and on the amount of free caesium released at the capsule, but also on the "bake-out" temperature. A temperature of about 275° C. has been found to be satisfactory for this purpose in which case the "bake-out" may extend for about 3 to 8 minutes. During this time and for a short time thereafter, the envelope is pumped until as much of the excess alkali metal as is possible, has been removed from the envelope. Some of the excess alkali metal will chemically combine with the lead glass stem and be permanently removed from the light-sensitive surface and from any other part of the electrode or envelope structure. The purpose of removing the excess alkali is to endow the tube with uniformity of operation, as is stated in the Bainbridge application, Ser. No. 244,533, filed January 4, 1928, in which claims to this feature have been made.

Following this treatment, the tube may be sealed off immediately from the pump, if a vacuum type tube is desired. However, instead of sealing off, argon or other inert gas may be introduced into the envelope at a pressure of about 125 microns. A glow discharge preferably is again produced between the electrodes, employing a direct current voltage of about 400 to 500 for this purpose with the anode 5 positive as in the prior glowing operation. The inert gas may be removed if a vacuum tube is desired but left in the envelope in the case of a gas-filled tube. It has been found that the sensitivity of vacuum and gas-filled tubes is greatly enhanced by the second glow treatment. The step of glowing the tube with inert gas as described immediately above, has been described and claimed in the Thomson application, Ser. No. 577,423, filed Nov. 27, 1931, and entitled "Photoelectric tubes".

From the foregoing, it is evident that I have improved on that portion of the manufacturing technique which concerns the oxidation of the cathode surface before the light-sensitive material is applied, and which may or may not be accompanied by heat. The improved treatment has been found to result in a much greater depth of oxide than that afforded by the usual heat treatment or oven method. In providing a greater amount of oxide, the cathode surface is enabled to occlude or adsorb, or both, greater amounts of light-sensitive material and thereby produce a greater degree of light-sensitivity. Furthermore, the electrical method of producing the oxide is susceptible of greater control and hence, of accuracy, than the prior methods used for this purpose.

What I claim as new and desire to secure by Letters Patent of the United States, is:

1. In the art of manufacturing photo-electric tubes which includes the steps of coating a foundation member with material which is readily oxidized, oxidizing said material and depositing thereon a layer of light-sensitive material, the method of performing the oxidation step which consists in subjecting the coated foundation

member to a direct current glow discharge while the member is exposed to oxygen.

2. In the art of manufacturing photo-electric tubes containing a light-sensitive cathode and an anode, said art including the steps of coating a cathode with silver, oxidizing said silver, and depositing thereon a layer of alkali material, the method of performing the oxidation step which consists in immersing the cathode and anode in an atmosphere of oxygen and applying a direct current discharge between the cathode and anode, said discharge being sufficient to cause a deep layer of oxide to form on the cathode surface.

3. In the art of manufacturing photo-electric

tubes containing a light-sensitive cathode and an anode, said art including the steps of coating a cathode with silver, oxidizing said silver, and depositing thereon a layer of alkali material, the method of performing the oxidation step which consists in immersing the cathode and anode in an atmosphere of oxygen and applying a direct current discharge between the cathode and anode with the positive voltage terminal of the discharge current supply connected to the anode and the negative terminal to the cathode, said discharge being sufficient to produce oxidation of the cathode surface.

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