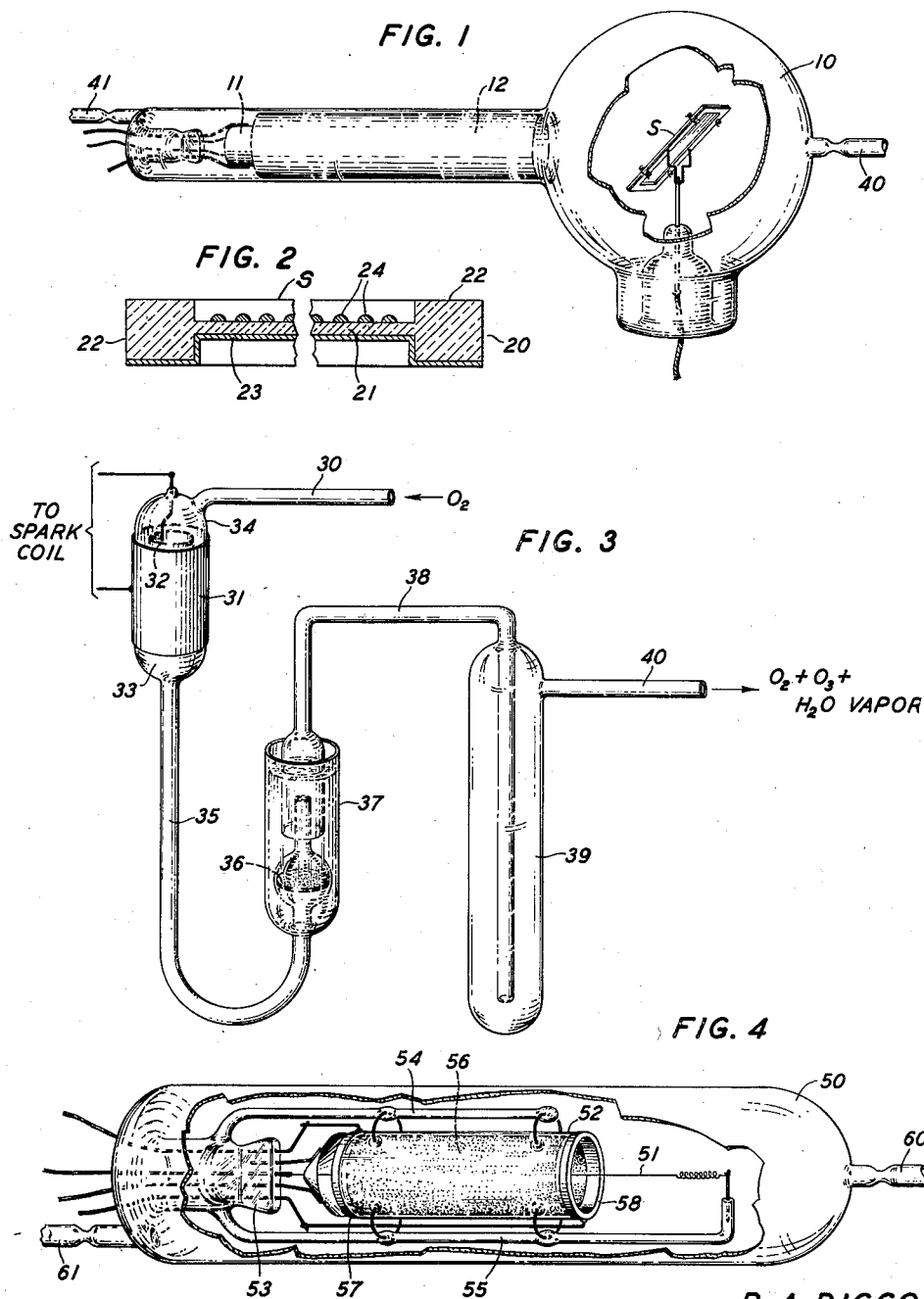


Feb. 6, 1940.

B. A. DIGGORY ET AL
ELECTRON DISCHARGE DEVICE

2,188,940

Filed Dec. 2, 1937



INVENTORS: B. A. DIGGORY
G. K. TEAL

BY

C. C. Sprague.
ATTORNEY

UNITED STATES PATENT OFFICE

2,188,940

ELECTRON DISCHARGE DEVICE

Benjamin A. Diggory, Plainfield, N. J., and Gordon K. Teal, New York, N. Y., assignors to Bell Telephone Laboratories, Incorporated, New York, N. Y., a corporation of New York

Application December 2, 1937, Serial No. 177,660

11 Claims. (Cl. 250—27.5)

This invention relates to methods of oxidizing metallic elements and to electrode structures, and more specifically to electrode structures in special types of electron discharge devices and to methods of oxidizing the electrodes in such devices.

In certain electron discharge devices such as, for example, photoelectric tubes, electronic camera tubes for television, and electron multipliers, electrodes having photosensitive surfaces are provided. In the preparation of these surfaces a metal face of the electrode is oxidized and then, in many cases, treated with a metal, such as silver, followed by photosensitization with an alkali metal.

In the preparation of some types of standard photoelectric tubes, the oxidation of the cathode is accomplished by the passage of an electric discharge through an atmosphere of oxygen between the cathode and anode of the tube. This oxidation method is successful in this instance because the electrode being sensitized is fairly symmetrically disposed relative to the anode, electrical contact can be made to it, it is mechanically strong, and it is made of silver, a material which is readily oxidized by electric discharge. Such conditions, however, cannot be simultaneously fulfilled in all photoelectric and secondary emission devices. Asymmetries in the electrode structure of a device are reflected in asymmetries in the electric fields and, where the oxidation is accomplished by means of charged particles, nonuniformity of oxidation of the electrodes may follow. In a device in which the electrode is insulated and to which an electrical connection cannot be made, it is impossible to pass a continuous current to it as is done in the discharge method described above. If the electrode to be oxidized is a thin metal film on glass, a continuous discharge passed directly to it usually tears it off the glass. Also, it is sometimes desirable to use metals other than silver as a base of a photoelectric or secondary emitting matrix and difficulty may then be experienced in oxidizing the metal by passing a discharge current to it in an oxygen atmosphere. For example, copper cannot be oxidized, at least not more than very superficially, by an electric discharge.

It is an object of this invention to provide novel electron discharge structures utilizing electrodes which behave differently in the presence of an oxidizing atmosphere.

It is a further object of this invention to provide a novel method of oxidizing metal struc-

tures which is particularly suitable for use in the preparation of electrode structures and photosensitive targets such as, for example, those used in television electronic cameras and electron multipliers.

In the method according to this invention as hereinafter described in detail by way of example, ozone (O_3) is generated by any suitable means such as, for example, by means of a spark coil and the gas allowed to flow through water vapor to moisten it. The moist ozone is then passed into the electronic camera tube or electron multiplier to oxidize the metal electrode or electrodes therein, the tube being heated to a temperature of about $50^\circ C.$ to prevent the water from condensing therein. After oxidation of the metallic electrode, the tube structure is baked out and evacuated at about $250^\circ C.$ Photosensitization of the oxide film follows this bake-out.

The invention will be more readily understood from the following description taken in connection with the accompanying drawing forming a part thereof in which:

Fig. 1 shows an electronic camera such as is used in television transmission in which the method of this invention may be applied;

Fig. 2 is an enlarged cross-sectional view of the mosaic screen or target of the tube shown in Fig. 1;

Fig. 3 shows apparatus for preparing the ozone used in the method of this invention; and

Fig. 4 shows an electron multiplier tube in which the method of this invention can be used.

Referring more particularly to the drawing, Fig. 1 shows an electronic camera tube used as a pick-up device in television transmission comprising an evacuated container 10 enclosing an electron gun assembly 11 for producing a moving beam of electrons and for accelerating this beam toward a screen S at the end of the tube remote from the electron gun, and means (not shown) for causing the beam to scan the various elemental areas of the screen S in turn.

As an example of a satisfactory electron gun assembly, reference may be made to Patent 2,173,923 to G. K. Teal, issued September 26, 1939, which shows and describes an electron gun comprising a cathode and two accelerating anodes for focussing a beam of electrons upon a target, one of these anodes being a conducting coating on the inside wall of the tube. A similar coating is shown in Fig. 1 of this application and is designated by the reference numeral 12. Either electrostatic or electromagnetic means (not shown) can be used for deflecting the

beam so that it scans every elemental area in turn of the screen S. Both of these means are well known to the art.

Reference will now be made to Fig. 2 for a more detailed description of the mosaic screen structure S. This screen structure has as a base a glass member 20 in the form of a very thin center portion 21 and a thicker edge portion 22. On the face of the glass member remote from the electron beam is evaporated a thin coating 23 of a suitable electrical conducting material, such as aluminum. On the surface of the center portion 21 nearer the electron beam is coated a discontinuous layer 24 of photosensitized metallic globules which is prepared by sputtering the center portion with a layer of metallic material such as silver, which is heated to make it discontinuous. The discontinuous globules are oxidized and caesium is introduced and the tube is baked to make the surface 24 photo-emissive.

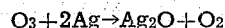
The preparation of the glass member 20 for use in the screen S will now be described. A piece of glass, preferably about .005 inch thick is etched by total immersion in a suitable etching solution, such as hydrofluoric acid, the edges of the glass being protected by a coating of a suitable substance which is not affected by the hydrofluoric acid, such as, for example, beeswax, so that the film of glass produced by the etching process has a border of glass of the thickness of the original glass plate by which it may be supported. For a more complete description of the method of preparing these glass screen members, reference may be made to the above-mentioned Teal patent wherein the process is described in detail.

After the glass blank has been prepared so that the center portion is as thin as desired and there is approximately a quarter of an inch of raised border all around the center portion, silver is sputtered on the center portion of one face of the blank for about 20 to 30 minutes. The silver layer is then heated to a temperature from 400 to 500° C. (usually between 425 to 450° C.) and then cooled. The heating causes the silver to break up into discrete globules. This process may be repeated one or more times in order to obtain a film of silver of the desired thickness. A platinum film is then formed on the entire back surface of the blank by sputtering. The blank is then mounted in the tube and the tube baked out and evacuated so that all the elements in the tube are thoroughly degassed. The tube is then ready for the oxidation process.

Referring now to Fig. 3 which shows a preferred form of apparatus for preparing moist ozone used in the oxidizing process, oxygen is introduced through the inlet 30 and passes between the electrodes 31 and 32 which are connected to a spark coil (not shown). The inside electrode 32 is an aluminum cylinder sealed into the pyrex glass tube 33 while the outside electrode is of copper foil attached to the external surface of the glass tube 33. The ozone formed in the silent discharge in the condenser chamber 34 is swept through the glass tube 35 and the sintered glass filter 36 and is saturated with water vapor by passing through the water in the reservoir 37. The moist gas is collected in the tube 38 and spray is removed from it by passage through the trap 39. The electronic camera tube is sealed to the ozone generator at the point 40. The water vapor in the ozone is prevented from condensing in the electronic camera tube by heat-

ing the latter to about 50° C. Failure to do this results in a non-uniform film of silver oxide. The excess ozone delivered from the electronic camera tube through tube 41 is prevented from entering the outside atmosphere by decomposition brought about by passage of the excess gases through a glass tube heated to about 550° C. (not shown).

The degree of oxidation of the silver film may be followed by determining its resistance as a function of time. When the resistance reaches a limiting value it is assumed that oxidation of the silver is approximately complete. Measurements made on the approximate ratio of silver to oxygen in silver films oxidized with moist ozone indicated approximate agreement with the formula Ag_2O . This indicates that the chief reaction occurring may be represented by the equation



Moisture is necessary to catalyze the reaction; without it, the oxidation proceeds with extreme slowness.

After oxidation of the silver film, the electronic camera tube is then baked out and evacuated at about 250° C. This temperature is sufficient to decompose the silver oxide completely if maintained for a sufficient length of time to fully establish equilibrium conditions. However, the approach to these conditions is rather slow and the amount of decomposition is made negligible by limiting the time of baking. If the ozone method of oxidation as described above is used, the metal portions of the tube should be made of materials not attacked readily by ozone. Aluminum metal, platinum, and chromium-plated nickel have been found to be fairly satisfactory in this respect.

At the conclusion of the oxidation process, excess gas is removed by evacuation and a known amount of caesium is emitted in the bulb by flashing a "caesium" pill. The pill is flashed in a side tube or in the bulb so that caesium vapor passes into the bulb to photosensitize the globules of the screen S. For a description of a process of photosensitizing with a "caesium" pill and the composition of such a pill, reference may be made to British Patent 381,606 to George R. Stilwell and Charles H. Prescott, Jr., complete accepted October 10, 1932. The tube may then be baked at a temperature of about 200 to 225° C. for varying degrees of time to remove all gases. For a further description of a tube having a mosaic photosensitive target of the type described herein together with a method of operation of a tube of this type, reference may be made to the above-mentioned Teal patent.

Fig. 4 shows an electron multiplier tube similar to that described by P. T. Farnsworth in the Journal of the Franklin Institute, volume 218, page 411 (1934). This electron multiplier comprises an envelope 50 enclosing an anode 51 and a cathode structure 52, both of which are supported from a press 53 by support members 54 and 55. The photo-cathode 52 is made by sputtering a very thin film of nickel on the inside of the glass cylinder 56 and then a semitransparent film of silver on the nickel film. Heavy rings 57 and 58 of platinum are sputtered on the inside at the ends of the cylinder to make contact with the silver film. The silver film is oxidized and then photosensitized. Several attempts using various other methods of oxidizing the silver were made prior to the use of the method according to this invention. An attempt was made to oxidize the

silver by passage of a direct electric current between the wire anode 51 and the cylinder 56 by the production of an oxygen gas discharge. In this attempt the silver film was made about 750 volts negative with respect to the anode 51. An attempt was also made to accomplish the oxidation by the passage of a high frequency gas discharge between the film on the glass cylinder 56 and the anode 51. In both cases difficulties were encountered because of the silver film being torn away from the glass. The oxidation was satisfactorily accomplished, however, by using the method of this invention.

The ozone vapor is admitted to the tube at the inlet 60 and passes from the tube through outlet 61. Tube 61 is sealed off at the conclusion of the oxidation but tube 60 is used to seal the envelope to the vacuum station. The process is similar to that described above in connection with the electronic camera.

It will be understood that this method is not limited to the preparation of electronic camera tubes or electron multipliers, but is of application in photoelectric tubes or in any other cases where it is desired to produce uniform oxidation and it is impossible to make electric contact to electrodes in the tube or other containing vessel. While the method has been described in connection with oxidizing silver it is to be understood that it is suitable also in connection with the oxidation of certain other metals, such as, for example, copper. The heating temperatures in the process where copper is used are likely to be higher than when silver is used due to the fact that copper oxide is more stable than silver oxide but otherwise the processes are similar. Other modifications and applications of the invention may obviously be made without departing from the spirit of the invention, the scope of which is defined by the appended claims.

What is claimed is:

1. The method of oxidizing an electrode structure to produce on said structure a uniform oxide layer of a thickness within predetermined limits, which comprises the steps of subjecting the electrode structure to moist ozone, and simultaneously heating the electrode structure to a temperature sufficient to prevent condensation of water vapor thereon.

2. The method of oxidizing an electrode structure to produce on said structure a uniform oxide layer of a thickness within predetermined limits, which comprises the steps of subjecting the electrode structure to moist ozone, and thereafter baking the structure.

3. The method of oxidizing a silver electrode structure to produce on said structure a uniform oxide layer of a thickness within predetermined limits, which comprises the steps of subjecting the silver electrode structure to moist ozone at a temperature of about 50° C., and thereafter baking the structure to a temperature of approximately 250° C.

4. The method of oxidizing a metallic electrode structure to produce on said structure a uniform oxide layer of a thickness within predetermined limits comprising the steps of introducing oxygen into a chamber wherein an electric discharge is produced to form therein ozone, passing the ozone through a reservoir having water therein to add water vapor to said ozone, removing the spray from said mixture by passage through a trap, and passing the resultant mixture which comprises oxygen, ozone and water vapor to the electrode structure.

5. The combination with a gas-tight container, of electrode elements therein, one of said elements being of material which oxidizes in the presence of moist ozone and another of material which does not so oxidize when subjected to moist ozone at the same temperature, means for producing a mixture of ozone and water vapor, and means for conducting said mixture to the interior of said container to produce an oxide coating on said element which oxidizes in the presence of moist ozone.

6. The combination with a gas-tight container, of an electrode of silver and a cooperating electrode of a material which does not readily oxidize in the presence of water vapor and ozone, means for producing a mixture of ozone and water vapor, and means for conducting said mixture to the interior of said container to produce an oxide coating on said silver electrode.

7. The method of oxidizing a plurality of electrode elements in a gas-tight container, one of said elements being of material which oxidizes in the presence of moist ozone to produce an oxide which is unstable when subjected to temperatures ordinarily employed in baking electrodes in electronic current discharge devices, and another of said elements being of material which does not so oxidize when subjected to moist ozone at the same temperature, which comprises the steps of mixing water vapor with ozone, conducting said mixture to the interior of said container and simultaneously therewith maintaining said electrodes at a temperature at which one of said elements will oxidize while the other of said electrode elements will not oxidize to produce an oxide coating on one of said electrodes.

8. The method of oxidizing an electrode element in a gas-tight container which electrode element is of a material which oxidizes in the presence of moist ozone, comprising the steps of mixing ozone with water vapor, conducting the mixture to the interior of the container to form an oxide coating on said element, and applying heat to said element while said mixture is being conducted into the tube sufficient to prevent condensation of water vapor thereon.

9. The method of oxidizing a metallic electrode structure to produce thereon a uniform oxide layer comprising the steps of passing ozone through water to add water vapor to said ozone, removing the spray from said mixture by passage through a trap, and directing the remaining mixture to the electrode structure.

10. The method of oxidizing a metallic electrode structure of a material which readily oxidizes in the presence of moist ozone to produce on said structure a uniform oxide layer of a thickness within predetermined limits, comprising the steps of producing ozone, mixing the ozone with water vapor, and passing the resultant mixture in controlled amounts to the electrode structure.

11. The method of oxidizing a metallic electrode structure of a material which readily oxidizes in the presence of ozone to produce on said structure a uniform oxide layer of a thickness within predetermined limits, comprising the steps of introducing oxygen into a chamber wherein an electric discharge is produced to form therein ozone, passing the ozone through a reservoir having water therein to add water vapor to said ozone, and passing the resultant mixture to the electrode structure.

BENJAMIN A. DIGGORY.
GORDON K. TEAL.