

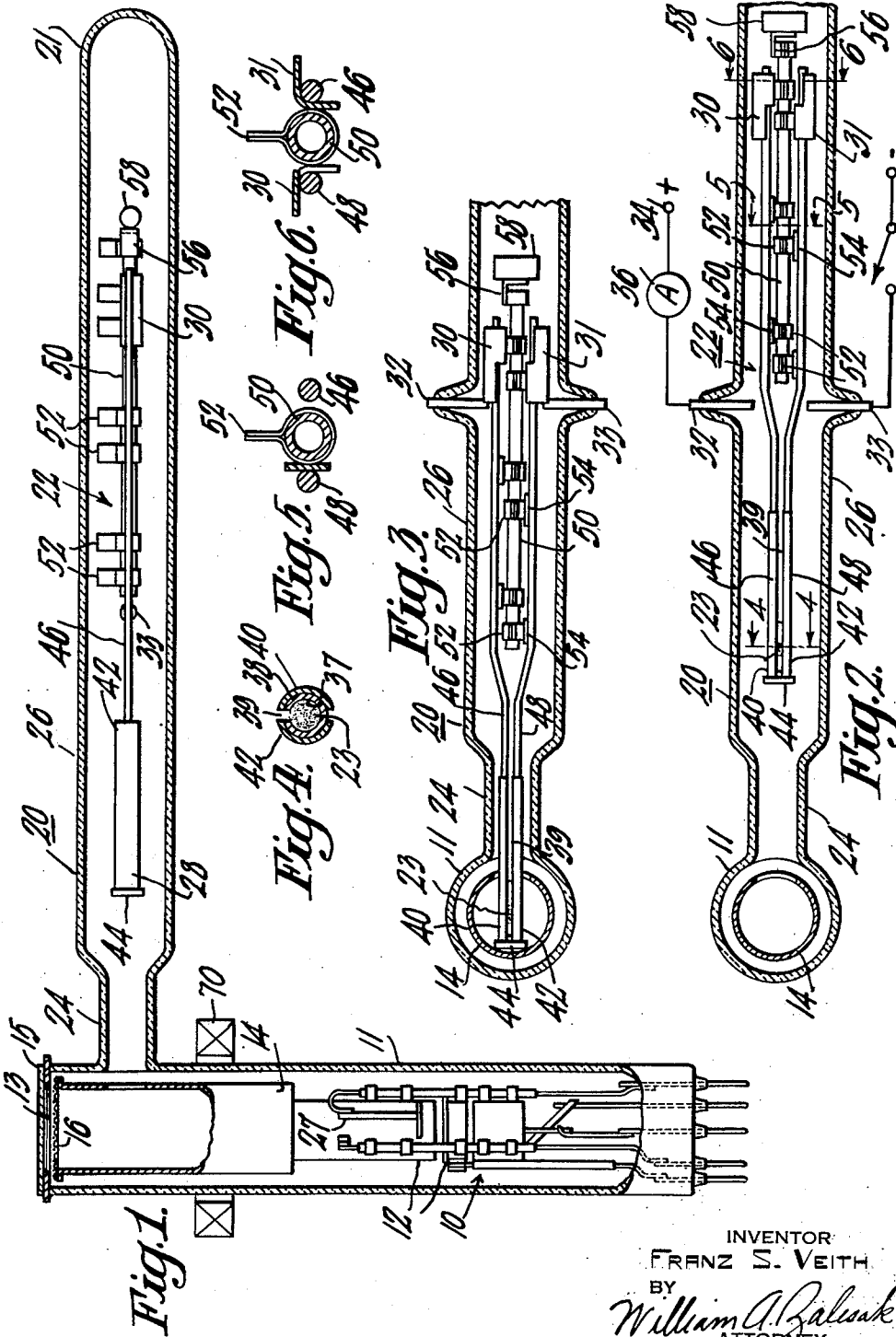
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PREPARATION OF POROUS PHOTOCONDUCTIVE LAYERS

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PREPARATION OF POROUS PHOTOCONDUCTIVE LAYERS

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This is a continuation-in-part of application Serial No. 279,746, filed April 1, 1952, now abandoned.

This invention relates to light-sensitive targets for electron discharge devices and particularly to an improved method of preparing such targets of the type having a layer of porous photoconductive material.

In the electronic arts, many devices such as camera pickup tubes of the vidicon or image orthicon types, phototubes and the like, utilize targets or photocathodes or other elements having layers of photoelectric material which may be deposited by an evaporation process. Broadly, a photoelectric material may be of the photo-emissive type or the photoconductive type. A photo-emissive material is one which emits electrons when the material is excited by light. A photoconductive material is one whose resistance to electrical current flow changes in response to light excitation. This invention is concerned with the preparation of a porous photoconductive layer, such as one made of antimony trisulfide.

The principles of the invention are of general application. However, they will be described with reference to the vidicon which employs a target layer of photoconductive material. The vidicon is described in an article in the RCA Review of September 1951 on pages 307 to 310 and in U. S. Patent No. 2,625,676 of S. V. Forgue. Vidicon camera tubes include an electron gun having a plurality of control electrodes including a mesh screen electrode and a target assembly contained in a glass envelope. The electron gun is similar to the conventional type used in the image orthicon and other cathode ray tubes. The target assembly comprises a film of light transparent electrically conductive material forming a signal plate on the glass face plate of the envelope and a layer of photoconductive material deposited upon the electrically conductive film. The target and the gun are so arranged within the envelope that an electron beam from the gun scans the photoconductive surface of the target.

The photoconductive material used for vidicon targets is an electrical insulator in the dark, but it becomes electrically conductive under the influence of light. The conductivity increases with the amount of light affecting the material, and is limited to the immediate area under the influence of the light.

Vidicons may be operated at either high or low velocity. That is, they may be operated with the signal plate at sufficient voltage positive with respect to the cathode so that the electron beam will strike the photoconductive layer with enough force to drive secondary electrons from the photoconductive material, thereby rendering it more positive. Or, they may be operated with the signal plate at a smaller positive voltage with respect to the cathode so that the scanning electron beam deposits electrons on the photoconductive layer with a negligible amount of secondary emission, thereby bringing the scanned surface of the photoconductor approximately to cathode potential.

In low velocity operation, the electrically conductive

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film or signal plate is connected to a voltage source which places the film at a positive potential with respect to the cathode which is at ground potential. Depending on the type of photoconductive material employed and the vacuum conditions within the tube envelope, the signal plate may be operated at a suitable voltage in the range of 5 to 200 volts. In one type of vidicon having an antimony trisulfide film evaporated in a gas atmosphere, the signal plate is biased at 40 volts positive. The electron beam scans the photoconductive surface and, by depositing electrons thereon at a velocity less than first crossover (i. e. where the ratio of the number of secondary electrons leaving the surface to the number of primary electrons striking the surface is less than unity), brings the bombarded surface to cathode potential and produces approximately a forty volt difference of potential across the target.

When light is focused upon an area of the target, it renders the photoconductive material conductive in that particular area, and causes the corresponding portion of the scanned surface of the photoconductive film to give up electrons and come a volt or so closer in potential to the conductive film. The next time the electron beam scans this area it restores to cathode potential the area from which electrons have leaked under the light-induced conductivity. This return to cathode potential restores the forty volt difference across the photoconductive layer and causes an electron current to the conductive film from the source of potential to which it is electrically connected. This electron current flows through an output resistor and provides the video signal output from the tube. In this type of operation, the screen electrode provides a uniform decelerating field for the electron beam as it approaches the photoconductive surface.

In one type of high velocity operation, the electron beam scans the photoconductive surface facing the electron gun at a velocity above "first crossover" (i. e. at a sufficiently high velocity so that the number of secondary electrons leaving the surface will be greater than the number of primary electrons which arrive at the surface to cause the secondary emission therefrom). The "first crossover" potential differs with different target materials and surface conditions. Two hundred volts between target and cathode has given satisfactory results with red antimony trisulfide targets.

The signal plate potential is applied to the electrically conductive film in contact with the opposite side of the photoconductor layer from the one scanned by the electron beam. A collector potential, which under some conditions of operation may be about ten volts positive with respect to the signal plate, is applied to a metal screen or ring, which in this case is termed the "collector electrode" and is located immediately in front of the scanned surface of the photoconductive layer. When the high velocity beam scans this surface, it releases secondary electrons which are attracted to the collector electrode, thereby making the scanned surface more positive until it reaches approximately the potential of the collector electrode and equilibrium is established between them. When the scanning electron beam has brought the scanned surface to collector potential, it makes that surface about ten volts positive with respect to the conductive film on the other side of the photoconductive layer.

When a light image is focused upon the target, the photo-conductive material becomes conductive in the areas where the light affects it. The effect of this conductivity is to cause a leakage of electrons from the conductive film, through the photoconductive layer, to the scanned surface. The amount of leakage depends upon the intensity of the light incident upon each area; and, its effect is to make the area of the scanned surface af-

ected by the light a volt or so less positive. When the scanning electron beam rescans an area from which the electron charge has leaked, it restores the charge. This leakage and restoration causes an electron current flow in a circuit between the light-transparent, electrically-conductive film in contact with the photoconductive layer and the source of potential to which it is connected. Variations in the electron current through this circuit, as more or fewer electrons are needed to restore the difference in potential, are the signal output of the tube.

In the manufacture of an electron tube having a photoconductive layer or film, such as the vidicon, the tube and its contents must be processed in conventional fashion by several operations including a baking step. The baking is employed to degas and dehumidify the tube envelope and its components. To accomplish effective baking the process must be carried out at comparatively high temperatures in the range of 400° C. to 450° C. Because most photoconductive materials suffer deleterious changes at these baking temperatures, the tube and its components are assembled and processed before the target area is coated with the photoconductive material.

Any suitable method may be used to deposit the layer of photoconductive material on the target area after the tube has been processed. According to one such method a side tubulation is attached to the envelope of the vidicon and an evaporator carrying the photoconductive material to be evaporated is inserted therein. The side tube is sealed off and with the evaporator in the retracted position, i. e. retained completely in the side tube and away from the tube envelope, the tube is exhausted and processed to completion. As mentioned above, the processing includes baking the tube and its components.

Next, the evaporator is moved into the tube envelope and the photoconductive material is heated and evaporated onto the target area. The heating of the evaporator to cause evaporation of the chemical material may be effected in any suitable manner, such as by baking the assembly in an oven, by high frequency induction heating or by direct electrical current flow through the evaporator. After the photoconductive material has been thus evaporated, the evaporator is retracted into the side tube and the side tube is pinched off and sealed.

By this method of preparation of the photoconductive film, some of the evaporated material is scattered and is deposited not only on the target area but also on the sides of the final accelerating electrode near the target and partly on the mesh screen electrode.

There are two principal disadvantages resulting from the deposition of photoconductive material on the screen collector electrode. If the deposition on the mesh screen electrode is sufficiently thick, some of the openings may be completely blocked. If this happens, the scanning electron beam cannot penetrate to the target and a distorted picture signal output results. Secondly, since the photoconductive material is an insulator, electrical charges are built up on the deposit on the mesh screen when it is scanned by the electron beam. Thus, the previously uniform electric field between the screen and the target is upset and the electron beam is not transmitted through the screen in uniform fashion. As a result the electron beam does not strike the photoconductive film uniformly and a distorted picture signal output results.

The deposition of photoconductive material on the screen may be avoided by effecting the evaporation under vacuum. However, there are some instances when it is desirable to evaporate the material in a gas to obtain a particular form of film such as one having a porous or fluffy texture.

Accordingly, the principal object of this invention is to provide an improved method of preparing an electron tube containing a target having a porous photoconductive film.

Another object of this invention is to provide an im-

proved method of preparing a target having a porous photoconductive layer.

In general, the objects and purposes of this invention are accomplished by evaporating a photoconductive material in the presence of a gas and onto a target area in conventional fashion to form a porous photoconductive layer. Scattered photoconductive material is then removed from the electrodes and other areas of the tube by means of localized heating of certain of the tube parts. The localized heating, in addition to removing the scattered photoconductive material, improves the sensitivity of the porous photoconductive layer.

Referring to the single sheet of drawings:

Fig. 1 is an elevational view, partly in section of a vidicon provided with the evaporator apparatus of the invention;

Fig. 2 is a plan view, partly in section, of the apparatus of Fig. 1 wherein an evaporator is in its retracted position;

Fig. 3 is a plan view, partly in section, of the apparatus shown in Fig. 1 with the evaporator in charge evaporating position;

Fig. 4 is a sectional view, through the evaporator only along the line 4—4 of Fig. 2;

Fig. 5 is a similar view along the line 5—5 of Fig. 2; and

Fig. 6 is a similar view along the line 6—6 of Fig. 2.

According to one suitable procedure for carrying out the principles of the invention, an electron tube envelope 11, for example, a vidicon envelope, is provided with an electron gun 10, including a suitable number of electrodes 12 and a final tubular accelerating electrode 14 having a mesh screen 16 mounted at one end thereof. A layer 13 of transparent conductive material, for example a layer of the type formed by pyrolytic deposition of a mixture of tin (stannic) chloride and methanol, is coated on the inner surface of the face plate 15 of the envelope 11. The photoconductive layer is not deposited on the conductive layer 13 at this time. The tube envelope 11 is also provided with a side tubulation or appendage 20 extending outwardly therefrom through which an evaporator 22 may be inserted. The side appendage 20 comprises a narrow cylindrical portion 24 and an expanded cylindrical portion 26.

After the aforementioned gun electrodes are mounted in the vidicon envelope 11, the evaporator is charged with a quantity of photoconductive material. Any suitable evaporator may be used for carrying the photoconductive chemical charge 23. One suitable device is shown in the U. S. Patent No. 2,733,115 of B. H. Vine and comprises a glass boat 38 having a chamber 37 and an opening 39 through which the photoconductive charge 23 is inserted into the boat and evaporated from the boat. The boat 38 is surrounded and supported by arcuate members 40 and 42 which are made of a resistance heating material such as a nickel-chromium alloy or the like. A conductive end piece 44 is connected across one end of each of the arcuate members 40 and 42 and the other ends of the members are connected to conductive rods 46 and 48. Such rods extend back from the arcuate members for a short distance and then diverge to provide a wider spacing between them. The divergent portions of the rods are retained and supported in insulated spaced relationship by a ceramic rod 50 which is fastened alternately to each conductive rod by means of brackets 52 and spacer elements 54.

Conductive wings 30, 31 are connected to the rods 46 and 48 respectively and a cylindrical slug 58 of magnetic material is fastened to the end of the ceramic rod 50 by means of a bracket 56. The magnetic slug is provided so that a magnet may be used in cooperation therewith to move the evaporator along the side tubulation.

The evaporator assembly 22 and its charge 23 of photoconductive material are inserted into the side tubulation 20 and the open end 21 thereof is sealed. The evap-

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orator is retained in retracted position near the sealed end of the side tube, and the envelope 11 and its included electrodes and other components are processed in conventional fashion. Thus retained in the retracted position, the photoconductive material 23 is maintained at room temperature and is not adversely affected by the tube processing steps.

In general, in being processed, the tube 11 is exhausted and baked to degas and dehydrate the envelope and its components. Baking may be effected by any suitable means, for example in a split oven (not shown) which comprises two arcuate oven portions which are positioned around the envelope 11. The tube is baked at a temperature in the range of 400° C. to 450° C. for about one hour. Next the getters 27 and electrodes 12 are degassed by a suitable procedure. Other processing steps may be included as required.

After the tube has been processed, the evaporator 22 is moved into the tube 11 until the leading end 28 contacts the inner wall of the accelerating electrode 14. In this position of the evaporator, the chemical charge 23 of photoconductive material is disposed within the tube 11 in position to be evaporated onto the target area, i. e. the inner surface of the face plate 15.

After the evaporator has been positioned within the tube, a gas is introduced into the tube to establish a gas pressure of approximately two to three millimeters of mercury. Such procedure is followed when the photoconductor is antimony trisulfide so that a porous, fluffy layer is deposited on the target surface. Such a layer or film results from collisions of the evaporated material with the gas molecules. Some inert gas such as argon is most satisfactory for use in evaporating antimony trisulfide since, in addition to promoting the formation of a porous layer, the inert gas prevents deleterious chemical reactions from occurring within the tube envelope. However, in some instances, air may be used as the gaseous atmosphere.

The evaporator is then heated. The evaporator described herein is heated by direct electrical current flow. According to this method, conductive pins 32 and 33 are mounted in the wall of the side tubulation 20 and are connected to a suitable source 34 of voltage. The evaporator is so constructed that when it is inserted into the tube envelope in position for evaporation of the photoconductive charge 23, the wings 30, 31 contact the pins 32 and 33 and an electrical current path is completed through the rods 46, 48, the arcuate members 40, 42 and the conductive end piece 44. Current flow through this path heats the resistive members 40, 42, the glass boat and its charge 23 and vaporizes the photoconductive charge out of the boat 38 through the opening 39 and onto the coated face plate 15. By this direct electrical heating of the evaporator, the current flow and the amount of heating are readily controlled. After evaporation, the evaporator 22 is retracted from the tube envelope into the side tube 20.

According to this evaporation procedure, some of the photoconductive material deposits on the inner coated surface of the face plate 15 as a porous or fluffy layer. However, some of the material also deposits on the mesh screen and on the wall of the tubular accelerating electrode 14. This is undesirable as described above because of the upset in the electron optics of the vidicon and resulting distorted signal output. In order to remove the photoconductive material from the wall of the electrode 14 and from the mesh screen 16 and in accordance with the invention, a high frequency coil 70 is positioned coaxially with the tube envelope just below the side tube. Approximately 40 amperes of high frequency current are passed through the coil and electrical currents induced in the tubular electrode 14 to produce heating therein. During this procedure the face plate 15 is kept cool by some suitable means as by a stream of cold air (not shown). This cooling means is provided to protect the

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photoconductive film which has been deposited on the face plate. As the electrode 14 is heated, the mesh screen 16 attached thereto is also heated and the scattered photoconductive material on the mesh screen 16 and on the walls of the electrode 14 are either re-evaporated onto the target or converted to a conductive form. This re-evaporation heating is generally applied for 40 to 60 seconds and the procedure is complete when the material on the mesh screen 16 is seen to disappear. Such treatment of the scattered chemical cleans up the screen so that it can function properly when the tube is completed and placed in operation. Another result of this re-evaporation procedure, in targets employing films of porous antimony trisulfide, is that a certain amount of heat radiates from the electrode 14 to the photoconductive film and readjusts the condensed photoconductive material so that a smoother film results. This readjustment improves the sensitivity of the photoconductive layer. It is to be understood that other heating devices may be used to remove the photoconductive chemical on the screen. For example, a split oven may be adapted to perform the desired function.

Next, the tube envelope is pumped out until the desired vacuum pressure is obtained. With the evaporator 22 completely retracted the side tube 20 is pinched off and the evaporator is removed. During this step, to prevent overheating, the face plate area is again kept cool by some suitable means (not shown), such as a stream of cool air or by means of a cap of wet asbestos and Dry Ice.

What is claimed is:

1. The method of forming a porous photoconductive layer on a predetermined target area within an electron tube envelope having a target support and an electron gun including a tubular accelerating electrode having a mesh screen electrode mounted at the end thereof adjacent to the target support, said method comprising the steps of evaporating photoconductive material in the presence of inert gas under low pressure through said mesh screen electrode to form a porous photoconductive layer on said target support, maintaining said target support and the photoconductive layer carried thereby at a temperature below that at which said photoconductive layer suffers deleterious changes, heating said tubular electrode while maintaining said target area at said reduced temperature, whereby the photoconductive material deposited on said tubular electrode and on said screen is removed by evaporation or changed to a conductive form.

2. The method of forming a porous photoconductive layer on a predetermined target area within an electron tube envelope having a target support and an electron gun including a tubular accelerating electrode having a mesh screen electrode mounted at the end thereof adjacent to the target support, said method comprising the steps of inserting photoconductive material within said tubular accelerating electrode, establishing an atmosphere of inert gas under low pressure within said envelope, evaporating said photoconductive material in the presence of said gas through said mesh screen electrode to form a porous photoconductive layer on said target support, maintaining said target support and the photoconductive layer carried thereby at a temperature below 400° C., heating said tubular electrode while maintaining said target area at said reduced temperature, whereby the photoconductive material deposited on said tubular electrode and on said screen is removed by evaporation or changed to a conductive form.

3. The method of forming a porous photoconductive layer of antimony trisulfide on a predetermined target area within an electron tube envelope having a target support and an electron gun including a tubular accelerating electrode having a mesh screen electrode mounted at the end thereof adjacent to the target support, said method comprising the steps of evaporating antimony trisulfide in a low pressure atmosphere of inert gas through said

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mesh screen electrode to form a porous photoconductive layer on said target support, maintaining said target support and the photoconductive layer carried thereby at a temperature below that at which said photoconductive layer suffers deleterious changes, heating said tubular electrode while maintaining said target area at said reduced temperature, whereby the photoconductive material deposited on said tubular electrode and on said screen is removed by evaporation or changed to a conductive form.

4. The method of forming a porous photoconductive layer of antimony trisulfide on a predetermined target area within an electron tube envelope having a target support and an electron gun including a tubular accelerating electrode having a mesh screen electrode mounted at the end thereof adjacent to the target support, said method comprising the steps of establishing an atmosphere of argon gas at a pressure of approximately two to three millimeters of mercury within said envelope, evaporating antimony trisulfide in the presence of said gas through said mesh screen electrode to form a porous photoconductive layer on said target support, maintaining said target support and the photoconductive layer carried thereby at a temperature below that at which said photoconductive layer suffers deleterious changes, heating said tubular electrode while maintaining said target area at said reduced temperature, whereby the photoconductive material deposited on said tubular electrode and on said screen is removed by evaporation or changed to a conductive form.

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5. The method of forming a porous photoconductive layer of antimony trisulfide on a predetermined target area within an electron tube envelope having a target support and an electron gun including a tubular accelerating electrode having a mesh screen electrode mounted at the end thereof adjacent to the target support, said method comprising the steps of evaporating said antimony trisulfide in a low pressure atmosphere of inert gas through said mesh screen electrode to form a porous photoconductive layer on said target support, maintaining said target support and the photoconductive layer carried thereby at a temperature below that at which said photoconductive layer suffers deleterious changes, heating said tubular electrode while maintaining said target area at said reduced temperature, whereby the photoconductive material deposited on said tubular electrode and on said screen is removed by evaporation or changed to a conductive form, there being sufficient heat radiated from said tubular electrode to said target area to produce a readjustment of the antimony trisulfide already deposited and an increase in photosensitivity.

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