Jan. 10, 1956 R. J. CASHMAN 2,730,638

PHOTOCONDUCTIVE ELECTRODE

Filed June 6, 1952

FIG. 1.

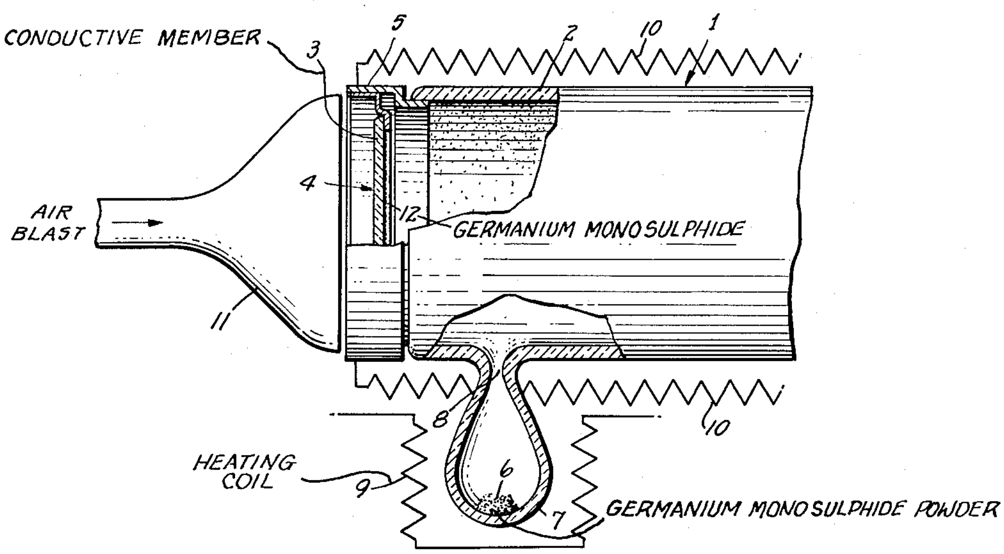
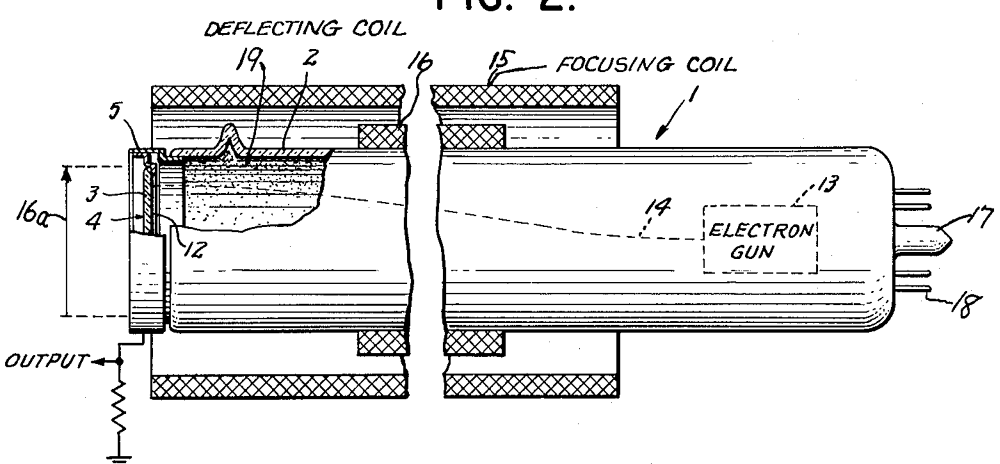


FIG. 2.



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PHOTOCONDUCTIVE ELECTRODE

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9 Claims. (Cl. 313—65)

This invention relates to photoconductive electrodes, particularly those adapted for use in television camera tubes.

While much work has been done in recent years on photoconductive type camera tubes, the results have not been altogether satisfactory. Major difficulties with such tubes have stemmed from the photoconductive material. Although many photoconductive materials are known and have been widely used, the requirements for such a material in a photoconductive camera tube are so special that none of the known materials satisfactorily meet these requirements. Some have too low a resistance to be used; some, like selenium, have too sluggish a response; some become "blocked" after exposure to high light intensities (i. e., become non-responsive) and a substantial amount of time is required before they recover and respond to variations in light. Other photoconductive materials have a limited range of intensity response and vary substantially in conductivity only over a relatively narrow portion of the range of light intensities. Similarly, there are materials whose conductivity changes rapidly between black and white making it difficult to electrically detect the grays in-between. Others have such an erratic response characteristic to different light intensities as to be unusable. Still other photoconductive materials only respond to light in a limited range of colors.

Other difficulties, too, have been encountered during operation of photoconductive camera tubes and during the manufacture thereof. For example, some photoconductive materials used in camera tubes have proven so unstable at higher temperatures that it has been necessary to use cooling fluids while operating said tubes. Other photoconductive materials have been difficult to handle during manufacture of the tubes, due, for example, to the fact that the photoconductive material could not be exposed to air as undesirable oxidation would ensue.

An object of the present invention is the provision of a photoconductive electrode, particularly one adapted for use in camera tubes, which uniquely combines different characteristics highly desirable in such tubes.

In accordance with a main feature of the present invention there is provided a photoconductive electrode consisting essentially of germanium monosulfide.

In accordance with another feature of the present invention, there is provided a photoconductive electrode consisting of a layer of conductive material of an extended area having a coating or layer of photoconductive material at least on one side thereof consisting essentially of germanium monosulfide.

In accordance with a further feature of the present invention, there is provided a photoconductive electrode of the type immediately hereinabove mentioned in which the conductive layer is light-transmitting so that light may be projected through said layer onto the photoconductive material.

In accordance with a still further feature of the present invention, there is provided a photoconductive electrode consisting of a conductive layer, a photoconductive layer essentially of germanium monosulfide on one side of said conductive layer and in electrical contact therewith over an extensive area, which photoconductive electrode is adapted to have a light image projected thereon to vary the conductivity of the germanium monosulfide material at different points thereon in correspondence with the variations of light intensity at different corresponding points of the light image, and which photoconductive electrode is further adapted to have the different points scanned to measure the variations in conductivity of these different points.

The above-mentioned and other features and objects of this invention and the manner of attaining them will become more apparent and the invention itself will be best understood by reference to the following description of an embodiment of the invention taken in conjunction with the accompanying drawings, wherein:

Fig. 1 is a schematic diagram of a portion of a camera tube, and apparatus associated therewith used in explaining one method of forming the photoconductive coating on the photoconductive electrode, and

Fig. 2 is a schematic diagram of a phtoconductive camera tube employing a photoconductive electrode in accordance with the present invention.

The photoconductive electrode made according to the present invention uses as its photoconductive material essentially germanium monosulfide. Germanium monosulfide, a known compound, may be formed from the elements germanium and sulphur by heating together sulphur and germanium in a vacuum to a temperature of 1000° C., substantially above the melting point of germanium. The relative weight of the sulphur and germanium used is proportional to their relative atomic weights, although a slight excess of sulphur, such as 1% has been employed without deleterious effects. When cooled, the resultant compound is a fused crystalline mass which may be crushed to a fine powder. This powder can be safely exposed to air without affecting the photoconductive properties of the electrode subsequently produced. Of course, the germanium monosulfide may be produced by other processes. It is believed that certain impurities may be present in the powder, such as a slight excess of sulphur or germanium and traces of oxide-containing compounds of germanium as well as possibly some slight traces of germanium disulfide. The presence of minute quantities of these impurities does not seem to affect the beneficial results obtained with the resultant photoconductive electrode and may even contribute to it. Essentially, however, the material employed consists of germanium monosulfide, and the impurities are preferably less than a small fraction of 1%.

In accordance with one aspect of the present invention, the germanium monosulfide, hereinafter referred to as the photoconductive material, is arranged in the form of a coating or layer of extensive area on a base member which is electrically conductive and has good light transmission characteristics so that light may be passed through the base portion and fall upon the photoconductive material.

While various techniques are known for arranging the coating on the base material, one simple method is as follows, reference being had to Fig. 1 in which the numeral **1** designates a camera tube having an envelope **2**, at one end of which there is mounted a transparent electrically conductive member **3** which may consist of a glass plate coated with a layer of transparent conductive material, member **3** serving as the base on which the photo-conductive material is coated, thus forming with the base **3** the photoconductive electrode **4**. The base **3** may be sealed to the end of the envelope **2** by means of a pair of Kovar rings **5**, one of said rings being sealed to an end of the envelope **2** and the other of the rings being sealed to the perimeter of the base 3, the two rings in turn being seam-welded together. The base 3 is transparent to light, and at the same time electrically conductive so that current passing through the photoconductive layer will pass readily through the base. One process of making such a base is described in U. S. Patent No. 2,566,346, the base consisting of glass with an electroconductive coating formed thereon. The photoconductive coating is formed on the base so as to be in contact with the electroconductive coating thereof.

The photoconductive powder prepared as hereinabove described and designated by the numeral 6 is placed in a little bulb 7 which is sealed to an opening 8 giving access to the interior of the envelope 2, in which the base 3 has been mounted as above described. The envelope 2 has been evacuated through another opening in the envelope thereof (not shown). The bulb 7 is then heated by a heating coil 9 to vaporize the photoconductive powder 6 which then passes through opening 8 into the envelope 2. For the purpose of causing the vapor to precipitate upon the base 3 and not on other parts of the envelope 2, the envelope 2 is heated by another heating coil 10 while the base 3 is cooled by an air blast directed against its outer surface through a funnel 11. A coating or layer 12 is thereby formed on the base 3 preferably of a thickness of .1 to 1 micron. The thickness of the coating may be controlled by passing light through the coating and observing it on the other side thereof. The temperatures are normally maintained in the range 400–500° C. during the sublimation of the powder. After the coating has been formed, the opening 8 is sealed off, usually leaving a surplus of material in the bulb. It is believed that the coating is principally amorphous although some crystalline structure may be interspersed randomly therein.

Further details of one known form of photoconductive tube that may use a photoconductive electrode according to the present invention is illustrated in Fig. 2 in which like numbers are applied to parts corresponding to similar parts in Fig. 1. The photoconductive tube 1 has a photoconductive electrode 4 of the type described in Fig. 1 mounted at one end thereof likewise as hereinabove described. Towards the other end thereof there is provided an electron gun 13 directing its beam 14 towards the photoconductive electrode 4. The beam is focussed magnetically by a focussing coil 15 and is deflected magnetically by a deflection yoke 16 so as to scan the elemental picture areas of photoconductive coating or layer 12. This scanning may be in rectilinear coordinates, that is, the usual vertical and horizontal scanning. On the operation of the tube, a light image from a source, for example, 16*a* is directed through the base portion 3 of photoconductive electrode 4 onto the photoconductive layer by suitable optical means (not shown). The effect of this light image is to vary the photoconductivity of the layer 12 at various portions of the area thereof in correspondence with the intensity of the light image at corresponding portions thereof. The electron beam then scanning the photoconductive layer produces a current flow through various portions of said photoconductive layer to the electro-conductive surface of base 3 which current varies in accordance with the conductivity of the photoconductive layer at that point. Further details illustrated in Fig. 2 consist of the tipped-off tubulation 17 used for evacuating the tube 1 and conductive leads 18 to the electron gun adjacent said tubulation. Electrical connection to the photoconductive electrode 4 may be made to the Kovar rings 5 secured to said electrode. A conductive wall coating 19 is also usually employed.

Tests were made on a photoconductive material as hereinabove described consisting essentially of germanium sulfide. It was noted that the photoconductive material has a high resistivity of about 10^{12} ohm-centimeters.

It can be exposed to air without damage and this stability in air makes it easy to handle and apply. It is also temperature-stable, that is, its photoconductive characteristics are not adversely affected by the temperatures encountered in the usual form of camera tube and no artificial cooling is required.

Experiments made with photoconductive camera tubes, of the general design hereinabove indicated, utilizing essentially germanium monosulfide for the photoconductive electrode made as described hereinabove, have shown the following advantages: It has been found that such tubes can be used for motion picture film scanning pickup because of the rapid response time which is at least of the order of $\frac{1}{30}$ of a second. These tubes produce a wide range of output in response to a wide range of variations of light intensity so that it becomes easy to recognize a large number of shades (of gray) between black and white, a highly desirable feature for such a tube. These tubes are not paralyzed or "blocked" (rendered unresponsive to subsequent light variations) by intense light and thus the question of recovery time does not arise. Further, the tubes respond well to variations in intensity of light covering a wide color range including the entire visible spectrum and extending somewhat beyond.

Of course, while there has been described a single method for preparing the photoconductive material, making the photoconductive electrode and a single type of tube in which it may be employed, it will be readily apparent to anyone versed in the art that different methods of preparing the photoconductive material, or making the photoconductive electrode may likewise be employed. Furthermore, while we have described a single transparent electroconductive base to be associated with the photoconductive material, it will be likewise apparent to those versed in the art that other transparent electroconductive bases may be formed or that in lieu thereof, an electroconductive base of poor light transmission characteristics may be employed and that the image might be impressed directly on the photoconductive layer without passing through the base as has been done, for example, by miscellaneous lens systems in the prior art, including that known as the "Schmidt" lens system. Furthermore, it will be apparent that the photoconductive electrode of the present invention may be employed in other types of tube, including also tubes using different scanning techniques other than those employing an electron beam.

Accordingly, while I have described above the principles of my invention in connection with specific apparatus, it is to be clearly understood that this description is made only by way of example and not as a limitation to the scope of my invention as set forth in the objects thereof and in the accompanying claims.

What is claimed is:

1. A photoconductive electrode for a tube in which a light image is converted into a corresponding electric signal comprising a conductive layer and a coating thereon in electrical contact therewith consisting essentially of germanium monosulfide.

2. An electrode according to claim 1 in which said conductive layer is light transparent.

3. An electrode according to claim 1 in which said coating has a thickness of the order of .1 to 1 micron.

4. An electrode according to claim 1 in which the coating has an electrical resistivity of the order of 10^{12} ohm-centimeters.

5. In a tube having a photoconductive electrode of extensive area adapted to receive a light image thereon to control the conductivity of different portions of the area thereof in accordance with the intensity of the light of corresponding portions of said image, and scanning means for passing current through different portions of said photoconductive electrode to measure the conductivity thereof; a photoconductive layer for said photoconduc-

tive electrode comprising essentially germanium monosulfide.

6. A radiation-sensitive device comprising an evacuated envelope, a cathode assembly supported in one portion of said envelope and an electron-producing device supported in another portion thereof; said cathode assembly comprising a conductive support having an image current-receiving surface and a film of germanium monosulphide on said surface, said germanium monosulphide being sensitive to radiation in the respect that its conductivity varies in accordance with the intensity of radiation projected thereon; and said electron-producing device providing a stream of electrons which impinge said film and which produce a current through said film corresponding to the latter's instantaneous conductivity at the point of electron impingement.

7. A radiation-sensitive device comprising an evacuated envelope, a cathode assembly supported in one portion of said envelope and an electron-producing device supported in another portion thereof; said cathode assembly comprising a conductive support having an image current-receiving surface and a film of germanium monosulphide on said surface, said germanium monosulphide being sensitive to radiation in the respect that its conductivity varies in accordance with the intensity of radiation projected thereon; said electron-producing device comprising an electron gun which emits a beam of electrons, and scanning devices for scanning said beam over said film, said beam cooperating with said film to produce a current therethrough corresponding to the conductivity of the film area impinged by said beam.

8. An electrode assembly comprising a conductive layer and a layer of photoconductive material in electrical contact with said member, said photoconductive layer being composed essentially of germanium monosulphide.

9. An electrode assembly comprising two layers of dissimilar material forming a plurality of elemental picture areas, one layer being composed of electrically conductive material and the other layer being composed essentially of germanium monosulphide, the elemental areas of said other layer being electrically connected respectively to said one layer.

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