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CAMERA TUBE TARGET INCLUDING POROUS PHOTOCONDUCTIVE LAYER COMPRISING ANTIMONY TRISULFIDE, FREE ANTIMONY AND COPPER PHTHALOCYANINE

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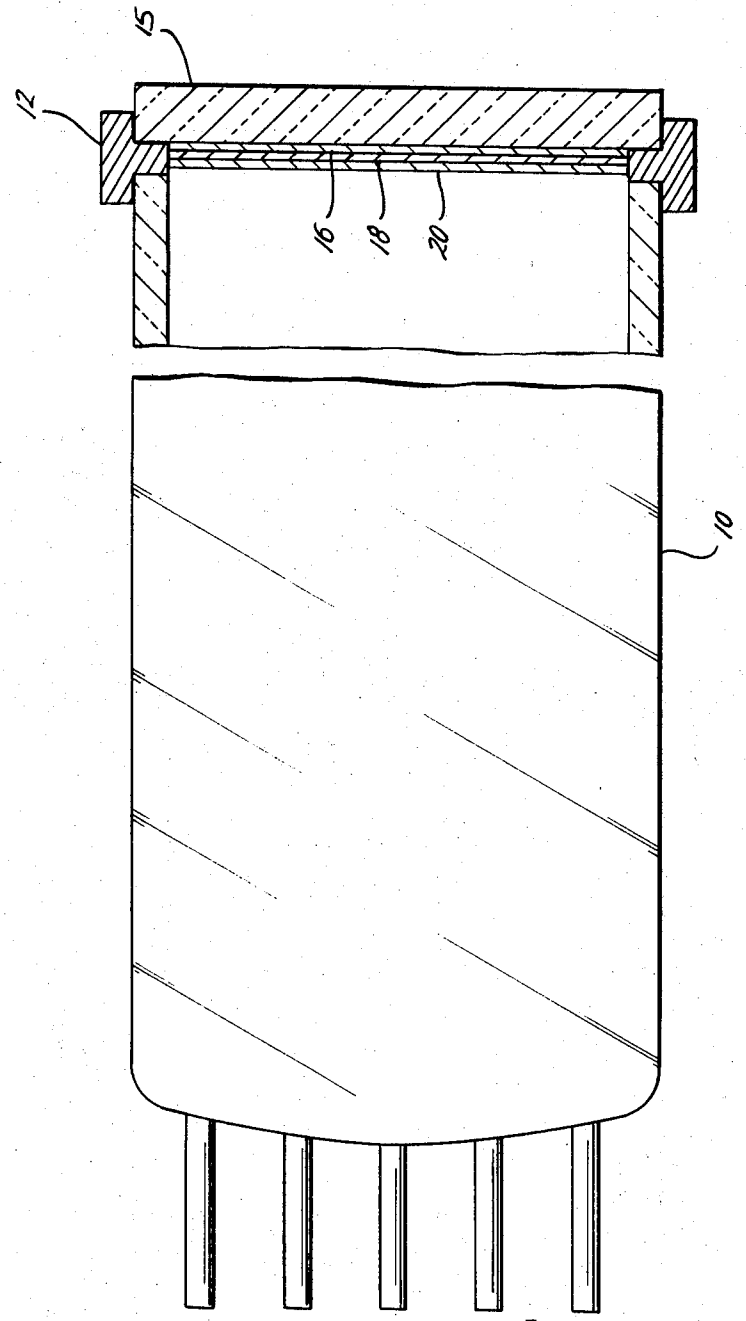

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CAMERA TUBE TARGET INCLUDING POROUS PHOTOCONDUCTIVE LAYER COMPRISING ANTIMONY TRISULFIDE, FREE ANTIMONY AND COPPER PHTHALOCYANINE

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Continuation-in-part of application Ser. No. 452,640, May 3, 1965. This application July 29, 1966, Ser. No. 568,823

1 Claim. (Cl. 313—65)

ABSTRACT OF THE DISCLOSURE

A television camera tube having a photosensitive surface containing an inorganic photoconductor and a minor proportion of an organic photoconductor, such as copper phthalocyanine.

This is a continuation-in-part of application Ser. No. 452,640, filed May 3, 1965.

This invention relates to electron discharge devices, and more particularly it relates to photoconductive targets for use in electron discharge devices, especially of the vidicon television camera tube type.

Vidicon tubes are well known in the television industry inasmuch as such vidicon tubes are in wide use, particularly in televising motion pictures. The general construction and operation of vidicon tubes are described on pages 22–22 and 22–23 of Radio Engineering Handbook, Fifth Edition, published by McGraw-Hill Book Company, Inc. A vidicon tube has a photoconductive coating applied to a support which is transparent to the radiation to be viewed, and which is made photoconductive by the imposition of a radiation image thereon. Electrons from an electron gun impinge upon the coating and create a signal which becomes the picture signal. It is well known that the functioning and operation of vidicon tubes can be greatly improved by close attention to the photoconductive coatings utilized in the targets.

As is well known in the art, photoconductive materials have comparatively high resistivities, but become conductive upon exposure to light. The sensitivity of such materials with various wave lengths of light is measured in microamps of current per unit of radiant energy impinging thereon. A coating of good sensitivity may have a sensitivity as high as from about 150 to 400 microamps per lumen.

A good vidicon target must also have a lag, or decay time, short enough for signals to be erased between scannings by the electron gun. In other words, the lag, or decay time, must be shorter than the time interval between two successive scannings of the same image element on the photoconductive coating. For the usual commercial television operation the lag should be short enough that the vidicon is capable of reproducing pictures of fast moving objects without a shadow or light trail. This requires a lag of something less than $\frac{1}{30}$ of a second.

Stanley V. Forgue has described, in his U.S. Patent 2,967,254, the preparation of a target for a photoconductive camera tube which comprises a conductive coating comprising a signal electrode applied to a light transparent window, a layer of a porous inorganic photoconductive material such as antimony trisulfide applied over the signal electrode, and a solid layer of an inorganic photoconductive material such as antimony trisulfide applied over the porous layer. As disclosed by Forgue, a porous layer is obtained by evaporating the material in a gaseous atmosphere at a comparatively poor vacuum of from about 2×10^{-1} to several mm. of mercury, while

the solid layer of material is deposited in a good vacuum of the order of 10^{-6} mm.

A major problem encountered in the use of vidicon tubes is known in the industry as "white burn-in." The phenomenon of "white burn-in" constitutes the forming of a negative after-image on the target of the vidicon. For example, in situations where the camera tube views a stationary scene for an extended period of time a negative image of this stationary sene may remain on the target and will show up on television display tubes. The reason for this white burn-in is not known, but it has been noted that modifications of photoconductive coatings to improve their sensitivities has resulted in a decrease of resistance to white burn-in. Thus, manufacturers of vidicon tubes have been unable to utilize photoconductive coatings of the highest sensitivities because of this objectionable feature.

The present invention, however, provides a photoconductive coating that has unusually good sensitivity with low lag but with less white burn-in than had heretofore been obtainable with the high sensitivity coating.

The superior performance of the photosensitive device of this invention is attained by using, with the usual inorganic photoconductor, a small proportion of an organic photoconductive material. It has been found that the use of such a minor proportion of organic photoconductor together with the usual inorganic photoconductors improves the sensitivity of the camera tube and decreases the lag time while substantially increasing the resistance to white burn-in.

Reference is now made to the accompanying drawing wherein the single figure portrays a vidicon camera tube with the target end shown in cross-section.

As shown in the drawing, the envelope **10** of the camera tube has attached thereto a metal ring **12** sealed to the end of the tube, the metal ring being made of a material such as Kovar. The end of the tube is closed by a light transparent face plate **15** which may be made of glass or quartz or the like, and which comprises a support for the target materials. In the embodiment shown in the drawing the target comprises a first conductive layer **16**, a second porous or spongy layer **18**, and a third solid vacuum deposited layer **20**.

The layers are preferably deposited by evaporation by means well known in the art and as explained for example, in the aforesaid patent to Forgue. As is also well known in the art, the conductive layer **16** may be any one of a number of known conductive coating materials such as for example, tin oxide or tin fluoride.

According to one embodiment of this invention, in preparing the spongy or porous layer **18** a mixture of organic and inorganic materials is evaporated in a poor vacuum onto the surface. One preferred mixture comprises antimony trisulfide, free antimony, and copper phthalocyanine, the free antimony in the mixture being about 10% of the weight of the antimony trisulfide, and the amount of copper phthalocyanine being about 5% of the antimony trisulfide-free antimony mixture. Following the deposition of this mixture in a spongy coating **18** on the signal plate coating **16**, a solid coating of antimony trisulfide, preferably contining about 15 parts by weight of free antimony per 100 parts of antimony trisulfide, is then evaporated onto the surface. Thereafter, the target is made more sensitive by heating, as is known in the art.

Although it is preferred to co-evaporate the organic and inorganic materials, substantially improved results in accordance with this invention can be obtained by separately evaporating the organic and inorganic photoconductors so that one of them forms a coating before the other one is evaporated onto the signal plate. Only a minor amount of the organic material is used, usually no

more than about 4% to about 10% of the weight of the inorganic photoconductor, so that the organic coating will be very thin as compared to the inorganic.

Copper phthalocyanine and other phthalocyanine dyes, such as aluminum phthalocyanine and chromium phthalocyanine, give good results in the composition of this invention. In addition, other organic photoconductors known in the art may be used to accomplish the unexpected results of this invention to a greater or lesser degree. Fused ring dye materials, such as anthracene and phenanthrene and other organometallic dyes, are included within such organic photoconductors. Preferably, materials are used which have a comparatively low vapor pressure.

It is noted that the use of the organic material combined with the inorganic photoconductive material substantially improves sensitivity and lag characteristics of the coating. The improved sensitivity is particularly significant in the red end of the visible spectrum. Furthermore, white burn-in is much less of a problem than with ordinary inorganic photoconductors used alone.

Although antimony trisulfide is the preferred inorganic photoconductor, other inorganic photoconductors known in the art, such as cadmium sulfide, cadmium selenide, and other sulfides and selenides as known in the art, may be used to practice the invention.

The addition of the organic photoconductors of this invention has been found to be particularly advantageous in a camera tube of the type described in Patent No. 3,003,075 to Krieger et al. Krieger particularly describes an image orthicon tube, although, as he points out, this photosensitive coating is also suitable for a vidicon tube.

The Krieger photosensitive device is designed for sensitivity to infra-red and contains a composite layer comprising lead oxide, sulfur and oxygen.

It has now been found that the sensitivity of the infra-red sensitive device of Krieger may be greatly improved by adding thereto an effective amount of an organic photoconductor such as, for example, copper phthalocyanine. For example, where a photosensitive target is made by the successive deposition of layers of lead oxide and sulfur, as described in the Krieger patent, if about 5% of copper phthalocyanine is also deposited, the sensitivity of the layer, particularly in the near infra-red area, is increased without detrimentally affecting the white burn-in of the target. Such a target has a peak sensitivity at about .9 microns, and the sensitivity range runs from about .55 to about 3 microns.

In applications in which copper phthalocyanine are used, it has been found that proportions of copper phthalocyanine less than about 4 parts by weight per 100 parts of the inorganic photoconductor have little or no effect upon sensitivity, lag, or white burn-in resistance of the coating. Furthermore, it has also been found that proportions higher than about 10 parts per 100 parts of the inorganic photoconductor actually cut down the sensitivity and makes a very grainy picture.

Many modifications and variations in this invention will be apparent to those skilled in the art, and therefore the invention is not limited to the embodiments shown and described herein but only as set forth in the following claim.

I claim:

1. A target for a photoconductive camera tube comprising

a signal electrode,

a porous photoconductive layer disposed substantially over one surface of the signal electrode,

and a solid photoconductive layer disposed substantially over said porous layer,

said porous layer comprising a mixture of antimony trisulfide, free antimony, and copper phthalocyanine, the amount of copper phthalocyanine being from about 4% to about 10% of the total weight of the antimony trisulfide and the free antimony.

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