# United States Patent [19]

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[11] **3,861,913** [45] **Jan. 21, 1975** 

3,355,289 11/1967 Hall et al
3,712,810 1/1973 Ciuffini
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[57] ABSTRACT
An electrophotographic plate comprising a conductive substrate, a charge transport layer and a charge gener- ation layer consisting essentially of from 5 to 35 per- cent by weight tellurium and from 0.5 to 20 percent
by weight arsenic, with the substantial balance being vitreous selenium.  6 Claims, No Drawings

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### **ELECTROPHOTOGRAPHIC CHARGE GENERATION LAYER**

#### FIELD OF THE INVENTION

The present application is concerned with electro- 5 photography. More paricularly it is concerned with a novel charge generation layer for use in electrophotographic plates. According to the present invention there is provided a charge generation layer consisting and from 0.5 to 20 percent by weight arsenic, with the substantial balance being vitreous selenium.

#### PRIOR ART

The use of vitreous selenium in electrophotography 15 is well known, as shown for example in U.S. Pat. No. 2,970,906. The addition of tellurium to selenium is shown in U.S. Pat. No. 2,745,327. The addition of arsenic to selenium is shown in U.S. Pat. No. 2,803,542. The three component material which is the subject of 20 the present application, however, it not disclosed in the prior art, and nothing in the prior art suggests the advantages obtained using a charge generation layer having the specified amounts of the three ingredients.

#### SUMMARY OF THE INVENTION

In electrophotography, the photoconductive insulator performs two functions, namely charge generation and charge transport. In the most commonly used processes, both functions are performed by a single layer, 30 for example a layer of vitreous selenium. These two functions may each be performed by a separate layer, and it is with such systems that the present invention deals.

The present invention provides novel charge genera- 35 tion layers for use in electrophotographic plates. These novel charge generation layers consist essentailly of from 5 to 35 percent by weight tellurium, and from 0.5 to 20 percent by weight arsenic, with the substantial balance being vitreous selenium. The most preferred  $^{40}$ composition is from 25 to 30 percent tellurium and from 2 to 10 percent arsenic. This three-component composition possesses unexpected advantages as a charge generation layer. In particular, it is extremely versatile. Depending upon the charging conditions and 45 upon the nature of the charge transport layer, the charge generation layers of the present invention can generate either electrons or holes. Furthermore, they are in some cases suitable for use on top of charge transport layers, and in other cases, beneath charge transport layers. In addition, the novel charge generation layers of the present invention may be used with either positive charging or negative charging.

The versatility of the charge generation layers of the present invention is such that they can, for example, be used to generate holes when they are positively charged as an overcoat for a vitreous selenium charge transport layer. In like manner, the charge generation layers of the present invention may be used to generate electrons when they are negatively charged and rest upon a layer of organic photoconductor such as described in U.S. Pat. No. 3,484,237 of Shattuck and Vahtra.

When the charge generation layers of the present inpolyvinylcarbazole or a layer of polyester containing oxadiazole, they are useful when charged in the negative mode. In like manner, the novel charge generating 2

layers of the present invention may be overcoated by a layer of polyester containing trinitrofluorenone and charged in the positive mode.

In some instances it may be of advantage to employ a vitreous selenium transport layer having as an interface with the charge generation layer a gradient composition comprising selenium and amounts of arsenic and tellurium which decrease with increasing distance from the charge generation layer surface. It is thus seen essentially of from 5 to 35 percent by weight tellurium 10 that, depending upon the proper choice of charge transport layer, the charge generation layers of the present invention may be either overcoated onto the charge transport layer, or overcoated by the charge transport layer, and may be charged in either the negative mode or the positive mode. This extreme versatility was totally unexpected, and constitutes one of the major advantages of the present invention.

The most outstanding advantage of the present invention is its very high sensitivity, over a very broad spectral range, when it is used as a charge generation layer with a suitable charge transport layer. An additional advantage of the present invention is that it is suitable for use on a wide variety of substrates, both rigid and flexible, and of many different shapes.

It is essential that the specified percentages of arsenic and tellurium be present. When less than 5 percent by weight of tellurium is contained in the charge generation layer, it loses sensitivity. On the other hand, when the tellurium concentration is above 35 percent, unacceptable dark decay occurs. Unless at least 0.5 percent by weight arsenic is present, surface crystallization of the layer may occur. On the other hand, when the arsenic concentration is greater than 20 percent by weight, the residual charge is too high.

In general it is preferred that the charge generating layers of the present invention be from about 0.02 to about 1.5 microns thick, most preferably from about 0.05 to 1.0 microns. In most cases, the charge transport layers will be much thicker, for example from about 8 to about 15 microns. When the charge transport layer is on top of the charge generation layer, the charge transport layer must be at least partially transparent.

When the charge generation layers of the present invention are used in electrophotographic plates, in most cases it is preferred that a suitable barrier layer also be employed. Many types of barrier layers are well known in the art. They serve the functions of holding the charge and preventing carrier injection from the conductor substrate. Barrier layers may be organic, for example, polyamide or polyurethane, or they may be inorganic, for example, aluminum oxide. In many cases the aluminum oxide film normally present on an aluminum conductive substrate is a suitable barrier layer.

The following Examples are given solely for purposes of illustration and are not to be considered limitations on the invention, many variations of which are possible without departing from the spirit or scope thereof.

# **EXAMPLE I**

A positive charging electrophotographic plate, which consists of an 1  $\mu$  Se (68 wt. %)-Te (30 wt. %)-As (2 wt. %) generation layer overcoated onto a 35 to  $50\mu$ vitreous Se transport layer on an anodized Al substrate, vention are overcoated with a charge transport layer of 65 is prepared by using vacuum evaporation. The substrate is held at a temperature near 70°C when the evaporations are conducted in a high vacuum system at a pressure of approximately  $1 \times 10^{-5}$  torr. The Se film

is vacuum deposited by heating the Se source to approximately 290°C for approximately 30 minutes. This is immediately followed by the deposition of the SeTeAs overlayer using flash evaporation of prealloyed granules. The crucible temperature for flash evapora- 5 tion of SeTeAs is normally maintained at about 500°C. A Sloan AMNI-II is used to monitor the deposit rates and film thicknesses of the Se and SeTeAs films. At the completion of the two consecutive depositions, the electrophotographic plate is cooled in situ to 25°C.

To assess image quality, this plate is corona charged to a positive potential of about 900 volts, and then exposed to a photocopy green light source at about 0.28 micro joules/Cm<sup>2</sup> to form a latent electrostatic image oped and transferred to a sheet of paper. A good quality image reproduced from the original is thus obtained.

Quantum efficiency measurements indicate that this electrophotographic plate exhibits a broad spectral response with peak quantum efficiencies up to 1, 0.8, and 20 0.5 at 4,000, 5,000 and 6,000 A respectively and shows weak field dependence of the quantum efficiency.

To check for surface crystallization, at  $1\mu$  Se (68 wt. percent) Te (30 wt. percent) As (2 wt. percent) film after an anneal treatment at 56°C for 88 hours is exam- 25 ined by X-ray diffraction. The results of detecting no crystallinity in the annealed film suggest the increased resistance to surface crystallization of the film due to the presence of As.

#### **EXAMPLE II**

A negative charging electrophotographic plate which consists of a  $0.1\mu$  Se (68 wt. %)-Te (30 wt. %)-As (2 wt. %) generation layer overcoated onto a  $10\mu$  transport layer of the organic photoconductor disclosed in 35 U.S. Pat. No. 3,484,237, on an aluminized Mylar substrate is prepared. (Mylar is duPont's brand of polyethyleneterephthalate.) the vacuum deposition of the SeTeAs film is carried out in the same manner as in Example I above except that in place of the 70°C substrate 40 temperature a substrate temperature of 45°C is used. This plate is corona charged to a negative potential of about 700 volts and exposed to a photocopy green light source at about 0.87 micro-joules/cm2 to form a latent electrostatic image on the plate surface. The electro- 45 static image is then developed and transferred to a paper. The image thus obtained shows excellent quality with minimal background.

# EXAMPLE III

A positive charging electrophotographic plate, which consists of an aliminized Mylar substrate, a  $0.3\mu$  du Pont Elvamide 8061 (polyamide) barrier layer, an 1  $\mu$ Se(68 wt. percent)-Te (30 wt. percent)-As (2 wt. percent) charge generation layer and a  $10\mu$  1 to 1 by 55 1 wherein the charge generation layer is covered by a weight trinitrofluorenonepolyester resin transport layer, is prepared. The SeTeAs charge generation layer is fabricated as in Example I above. The transport layer is prepared by dissolving the 2, 4, 7-trinitrofluorenone (TNF) in tetrahydrofurane (THF) solvent with the 60 Goodyear Vitel PE-200 polyester resin. Application of the transport layer, overlaying on the SeTeAs genera-

tion layer, is normally accomplished by using a meniscus coating technique.

This electrophotographic plate is corona charged to a positive potential of about 750 volts and exposed to a photocopy green light source at about 0.41 micro joules/cm<sup>2</sup> to form a latent image on the plate surface. This latent image when developed and transferred to a paper, shows excellent quality with little background.

# **EXAMPLE IV**

A positive charging electrophotographic plate is prepared as in Example III above except that in place of the  $1\mu$  Se(68 wt %)-Te (30 wt. %)-As (2 wt. %) film, an  $1\mu$  Se(70 wt. %)-Te (20 wt. %)-As (10 wt. %) is on the plate surface. The latent image is then devel- 15 used as the generation layer. This plate is corona charged to a positive potential of about 700 volts. Upon exposure to a tungstenhalogen liggt source at about 0.89 micro joules/cm2, the plate is observed to discharge to a potential of about 200 volts.

# EXAMPLE V

A negative charging electrophotographic plate, which consists of an anodized Al substrate, an  $1\mu$  Se (73 wt. %)-Te (25 wt. %)-As (2 wt. %) charge generation layer and a 11 $\mu$  PE 200 polyester (49.75 wt. %)-2,-5-bis-dimethylamine-p-phenylene-1,3,4 (49.75 wt. %)-TNF (0.5 wt. %) is prepared as in Example III above. This plate is negatively corona charged and then exposed, developed and the toned image transferred in the same manner as the plate in Example III. The image thus obtained shows good quality with a slight background. Quantum efficiency measurements indicate that this plate shows a broad spectral response with peak quantum efficiencies up to 0.56, 0.54 and 0.29 at 4,500, 5,000 and 6,000 A respectively.

What is claimed is:

- 1. An electrophotographic plate comprising a conductive substrate, a charge transport layer, and a charge generation layer consisting essentially of from 5 to 35 percent by weight tellurium and from 0.5 to 20 percent by weight arsenic, with the substantial balance being vitreous selenium.
- 2. An electrophotographic plate as claimed in claim 1 wherein the charge generation layer comprises from 2 to 10 percent by weight arsenic and from 25 to 30 percent by weight tellurium.
- 3. An electrophotographic plate as claimed in claim 1 wherein the charge generation layer covers a charge 50 transport layer of vitreous selenium.
  - 4. An electrophotographic plate as claimed in claim 1 wherein the charge generation layer covers a charge transport layer comprising an organic photoconductor.
  - 5. An electrophotographic plate as claimed in claim charge transport layer comprising polyester resin and trinitrofluorenone.
  - 6. An electrophotographic plate as claimed in claim 1 wherein the charge generation layer is covered by a charge transport layer comprising oxadiazole and a polyester resin.