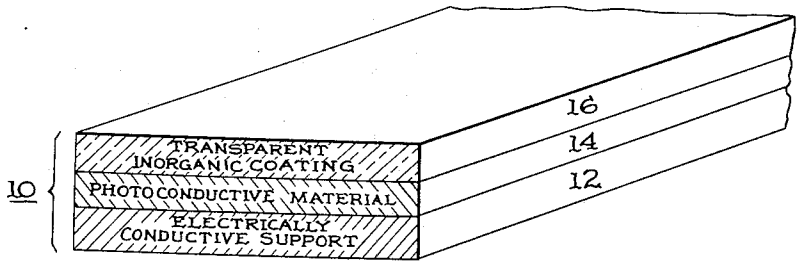
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PROTECTED PHOTOCONDUCTIVE ELEMENT AND METHOD OF MAKING SAME

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PROTECTED PHOTOCONDUCTIVE ELEMENT AND METHOD OF MAKING SAME

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This invention relates to a novel photoconductive material possessing an outstanding combination of properties. More particularly, it relates to a photoconductive element comprising at least one portion formed of a photoconductive material having a high sensitivity and a second portion forming a transparent protective overcoating disposed on the first portion and serving to protect it from chemical and physical attack during its use.

Recent activity in the field of photoconductive television pick-up tubes, electrostatic photography and electrostatic printing has heightened interest in high resistance photoconductive materials. Among the high resistance photoconductive materials which have been employed in the prior art are elemental amorphous selenium, combinations of selenium and arsenic, activated zinc sulfide, and activated zinc-cadmium sulfides. Although each of these materials has an extremely high resistivity in the dark, generally of the order of 10^{12} ohm centimeters or greater, and a resistance decrease factor of about 100 or more when illuminated, and each of these materials further possesses some particular characteristic which suggests its use in certain limited applications, some limitation in each material serves as a deterrent to its widespread use in electrostatic photographic devices.

Of the above noted photoconductive materials, senenium and combinations of selenium with small but significant amounts of additional materials, including arsenic and various oxides and sulfides, have been found to possess a sensitivity to visible light greater than that of any of the other known photoconductive materials having the necessary high resistivity and resistance decrease factor required for their application to electrostatic printing processes presently practiced. From a practical point of view, however, selenium based photoconductors have been found to possess at least two important disadvantages in the intended application. The materials have been found to be relatively soft and to wear poorly when subjected to charging, developing and cleaning operations of electrostatic photographic operations. Furthermore, the selenium based photoconductive materials heretofore developed have been found to be susceptible to chemical attack as well as physical wear during their repeated use in electrophotographic processes with a resultant significant alteration of their properties after repeated use. One property which changes in a particularly undesirable manner is the dark resistance, which is substantially diminished after repeated use.

One type of prior art electrostatic photographic process is exemplified in Carlson Patents 2,297,691 and 2,357,809 among others. In accordance with this process a relatively durable layer of a photoconductive material, based on sulfur, anthracene or anthraquinone is electrostatically charged by rubbing and after a latent electrostatic image is formed in the charged layer, the image is developed by means of an opaque solid powder. In order to reuse the photoconductor, it is necessary to remove the powder. In practicing the Carlson process it has been found that when a higher sensitivity photoconductor such as

the selenium based compositions above noted is employed, the charging procedure, image development, image transfer and subsequent cleaning operations all are severely abrasive on the soft photoconductor.

In other prior art electrostatic photographic processes, the severely abrasive action of the opaque particulate material employed to develop a visible image from a latent electrostatic image is somewhat diminished through the use of liquid developer compositions. By appropriately modifying the charging procedure, the initial charge may be imparted to the photoconductive layer by other means than the severe rubbing technique disclosed in the Carlson patents. But in any event, the softer photoconductive materials, particularly those based on selenium, have been found to be subject to scoring and to rapid wear and to chemical attack in service.

It is one object of this invention to provide a means whereby selenium based photoconductive materials may be employed in the electrostatic photographic processes of the prior art without the disadvantages hitherto encountered.

It is another object of this invention to provide a photoconductive element which has a relatively high sensitivity and which is more resistant to both physical and chemical attack than selenium based photoconductive materials.

A further object of this invention is to improve the performance of selenium based photoconductive materials in repetitive electrostatic printing processes.

Still a further object of this invention is to provide a method of protecting a high sensitivity photoconductive material without any substantial impairment in the sensitivity of the material.

These and other objects will become readily apparent to those skilled in the art from a consideration of the specification and claims which follow.

The single figure shows a fragment of a xerographic plate prepared in accordance with the present invention. As shown, the improved xerographic element **10** comprises a layer **14** of a photoconductive insulating material such as selenium, supported on an electrically conductive base **12** and covered by a thin transparent layer **16** of an inorganic insulating material as described below. It will be understood that the several layers are shown schematically and that their actual thicknesses may vary widely provided certain requirements described below are observed.

I have discovered that the advantages associated with the use of selenium and compositions in which selenium comprises the major constituent as photoconductive elements in an electrostatic photographic process may be preserved by protecting the sensitive photoconductive material with a thin transparent film of a material having electrical characteristics selected so as to match those of the photoconductive material. More particularly, I have found that the soft and relatively susceptible selenium photoconductive compositions may be protected against abrasive wear and against chemical attack by providing a thin transparent layer of a high resistance material having a resistance characteristic substantially at least equal to the dark resistivity of the selenium photoconductive composition. Many insulating materials possessing the desired resistance are known. For example materials possessing the necessary electrical characteristics in combination with the required durability include zinc sulfide, silica, titania, various silicates, alkaline earth fluorides and indeed any other insulator with the required properties provided it may be deposited in intimate contact with the selenium base photoconductor.

Depending on the relative thickness of the undercoat and the overcoat, the composite produced may possess as much as 90% of the sensitivity of the undercoat alone. For the present intended use in electrostatic photography,

the selenium or selenium base photoconductive composition layer should be at least 0.05 mil in thickness and preferably not over 1 mil thick.

The thickness of the insulating overcoating will depend to some extent upon the specific material selected. The maximum permissible thickness is one at which the overcoat no longer transmits sufficient visible light to impart the necessary conductivity to the photoconductive layer. The minimum thickness is one at which the overcoat fails to provide the desired protection from chemical as well as physical influences.

I prefer to employ zinc sulfide as a protective coating. With this material it has been found that the overcoating should be of a thickness corresponding to about one tenth of the thickness of the photoconductive layer. With thicknesses of 0.05 to 1 mil in the photoconductor, I have found that the coating layer should preferably range from 0.01 to 0.1 mil in thickness. Where thicknesses of the overcoat greater than those specified are employed, I have found that the sensitivity is markedly decreased. On the other hand with overcoatings which are too thin, the desired protection is not achieved.

I have found that the protective coating may be applied to the photoconductive layer in a variety of ways, without adversely affecting the sensitivity of the resultant composite, provided that the protective coating is in intimate physical and electric contact with the photoconductor. Thus the overcoating may be applied by spraying, by simply brushing or painting, or in the case of a readily vaporizable substance such as zinc sulfide, the coating may be deposited in the form of a thin uniform film by evaporation onto the photoconductive subtrate in a vacuum, in a manner similar to that well known in the art for depositing phosphor layers of zinc sulfide.

I have further observed that the sensitivity of the composite may be considerably enhanced when selenium or selenium based photoconductors protected by a zinc sulfide overcoat are heat treated after they have been prepared. Thus after heat treatment at 200° C. in air for about 90 minutes, the sensitivity of a composite comprised of arsenic solenide ($AsSe_3$) overcoated with zinc sulfide was increased by a factor of 2½ when expressed as the percentage charge loss with a given exposure to a standard light source, while another composite similarly prepared except that the heat treatment was effected in air at 150° C. for 90 minutes showed an increase by a factor of 5. Heating for between 1 and 2 hours in an oxidizing atmosphere such as air to temperatures ranging from 80° C. to 200° C. has been found to materially improve the properties of the product obtained.

Composites prepared in accordance with my invention have been found to possess a substantially longer service life before they deteriorate sufficiently to render them unsuitable in electrostatic photographic processes such as those described.

While I have referred specifically to a composition of selenium containing arsenic in the proportion corresponding to the compound $AsSe_3$, many other proportions have been found to possess the desired properties. Accordingly the expression "arsenic selenide" as used in the following claims is intended to include selenium with arsenic in any effective amount up to equimolar ratios, as disclosed in a copending application, Serial No. 419,562 of which I am a joint inventor and which issued February 4, 1958, as United States Patent 2,822,300.

One further point remains to be noticed and this concerns the insulator covering the relatively soft selenium base photoconductor. While it is necessary that this overcoat be chosen from materials having a dark resistivity, at least substantially equal to the selenium photoconductor, it does not follow that the material cannot also be photoconductive. Indeed, in some instances, it will be preferable to employ a photoconductive covering material in the form of a thin transparent layer whereby the composite will possess photoconductivity resulting from both layers.

I claim:

1. A photoconductive member for use in electrostatic photography consisting of (*a*) an electrically conductive support layer; (*b*) an intermediate layer of photoconductive material having a resistivity in the dark of at least about 10^{12} ohm centimeters and a resistance decrease factor of at least about 100 when illuminated, integral with said electrically conductive layer and supported thereon; and (*c*) a protective transparent homogeneous coating between 0.01 and 0.1 mil thick, integral with said photoconductive layer and composed of inorganic material selected from the class consisting of electrically insulating inorganic materials having a resistance characteristic substantially at least equal to the dark resistivity of the photoconductor and selected from the group consisting of ZnS, SiO_2, TiO_2 and alkaline earth fluorides.

2. A photoconductive element for use in electrostatic photography consisting of an electrically conductive support layer; a photoconductive layer comprising photoconductive amorphous selenium, integral therewith and supported thereon; and a protective transparent and homogeneous layer of between 0.01 and 0.1 mil of zinc sulfide integral with and overlying said photoconductive layer.

3. A photoconductive element for use in electrostatic photography consisting of an electrically conductive support layer; a photoconductive amorphous selenium layer integral with and supported thereon; and a protective transparent electrically insulating layer consisting of inorganic material having a resistance characteristic substantially at least equal to the dark resistivity of the photoconductive layer and selected from the group consisting of zinc sulfide, silica, titania, and alkaline earth fluorides.

4. A photoconductive element for use in electrostatic photography comprising in combination an electrically conductive support layer; a photoconductive layer supported thereon and integral therewith and consisting essentially of photoconductive amorphous selenium in a thickness of at least 0.05 mil and not over 1.0 mil; and supported thereon and integral therewith, a transparent layer of zinc sulfide between 0.01 mil and 0.1 mil in thickness.

5. In an electrophotographic process in which a visible image is formed from a latent electrostatic charge pattern borne by a photoconductive insulating material, the improvement which comprises: providing as the latent image bearing element an electrophotographic member consisting of an electrically conductive support layer, a layer of photoconductive material comprising amorphous photoconductive selenium supported on and integral with the electrically conductive layer and a protective transparent homogeneous layer of zinc sulfide overlying said photoconductive insulating layer and integral therewith; and developing a visible image on said electrophotographic member by bringing a xerographic developer into physical contact with the thin transparent protective layer of zinc sulfide when said electrophotographic member bears a latent electrostatic image.

6. The process of claim 5 in which the thin transparent protective layer formed of zinc sulfide is between 0.01 and 0.1 mil thick.

7. A method of preparing an improved photoconductive element for xerography which comprises: vacuum depositing on an electrically conductive base, a film consisting essentially of photoconductive amorphous selenium and having a thickness of between about 0.05 mil and 1 mil and a resistivity in the dark of at least 10^{12} ohm-centimeters; and depositing on said selenium layer, a thin transparent homogeneous layer of zinc sulfide having a thickness of between 0.01 and 0.1 mil, integral with the selenium layer.

8. A method of improving the useful life of a re-usable

xerographic plate consisting of a photoconductive insulating material on an electrically conductive base which comprises providing a protective transparent layer integral with and in physical contact with said photoconductive insulating layer, and consisting of a layer between 0.01 and 0.1 mil thick an inorganic electrically insulating material having a durability substantially greater than that possessed by the photoconductive insulating layer and selected from the group consisting of zinc sulfide, silica, titania and alkaline earth fluorides.

9. The method of claim 8 in which the transparent layer is zinc sulfide.

10. The method of claim 9 in which the xerographic plate is heated in air to temperatures between about 80° C. and 200° C. for up to about 2 hours.

11. A heat treated photoconductive element comprising a photoconductive material consisting essentially of amorphous selenium wherein the said photoconductive material is provided with a transparent coating of zinc sulfide between 0.01 and 0.1 mil in thickness secured to and integral with said selenium, said element having been subjected to heating in air for about 1½ hours at a temperature between 80° C. and 200° C.

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