

[54] SURFACE TREATMENT OF ARSENIC-SELENIUM PHOTOCONDUCTORS

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[58] **Field of Search**..... 96/1.5, 1.5 C; 117/201,
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[57] **ABSTRACT**

A method of improving the electrical characteristics of an arsenic-selenium photoconductive layer is disclosed which comprises coating the surface of said layer with a specific thickness of an organic material which is selected from the group consisting of a mixture of vinyl chloride and vinyl acetate, chloranil, the tributylamine salt of styrene-methacrylic acid, 2,4,7-trinitro-9-fluorene, p-benzoquinone, naphthylamine, hexachlorobenzene, polyvinyl carbazole, N-vinyl carbazole, N-N-dimethylallylamine anthracene, aniline hydrochloride, mesitylene and phenoxy resins. Coating with these materials prevents surface charges contained on the photoconductive layer from injecting into the bulk of the photoconductor, thereby reducing the dark discharge characteristics of the photoconductor.

5 Claims, No Drawings

SURFACE TREATMENT OF ARSENIC-SELENIUM PHOTOCONDUCTORS

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of application Ser. No. 204,477, filed Dec. 3, 1971, now abandoned which in turn is a continuation-in-part of my previous application, Ser. No. 888,030, filed Dec. 24, 1969 now abandoned.

In the art of xerography, a photosensitive element containing a photoconductive insulating layer is first uniformly electrostatically charged in order to sensitize its surface. The plate is then exposed to an image of activating electromagnetic radiation such as light, X-ray, or the like, which selectively dissipates the charge in the illuminated areas of the photoconductive insulator while leaving behind a latent electrostatic image in the non-illuminated areas. This latent electrostatic image may then be developed and made visible by depositing finely divided electroscopic marking particles on the surface of the photoconductive insulating layer. This concept was originally disclosed by Carlson in U.S. Pat. No. 2,297,691, and is further amplified and described by many related patents in the field.

The use of vitreous selenium, as taught by Bixby in U.S. Pat. No. 2,297,907, introduced to commercial xerography a photoconductor capable of holding and retaining an electrostatic charge for relative long periods of time when not exposed to light. In addition, vitreous selenium exhibits relatively good sensitivity to light as compared to other photoconductive materials and has sufficient strength and stability to be reused hundreds or even thousands of times.

U.S. Pat. Nos. 2,803,542 to Ullrich and 2,822,300 to Mayer et al both disclose improvements over vitreous selenium by the incorporation of elemental arsenic in amounts ranging from less than 1 percent to about 50 percent by weight. The addition of arsenic has been found to increase the stability of selenium with regard to crystallization, and additionally provides increased spectral response in the yellow-red band of the electromagnetic spectrum to which vitreous selenium is relatively insensitive.

In a typical xerographic cycle, a given plate is charged in the dark to a particular potential called the "acceptance potential." After the plate has been charged, a certain percentage of the acceptance potential is lost in the absence of light. This loss in apparent surface voltage is called "dark discharge" or "dark decay." If the dark discharge becomes a significant percentage of the initial acceptance potential, it can be seen that only a portion of the initially accepted potential will eventually be available for development of a latent electrostatic image after the plate has been exposed to a pattern of light. It can therefore be seen that the dark discharge for a given xerographic plate should preferably be kept at a relatively low level in order that a maximum amount of voltage be available for the development of the electrostatic image. In modifying or improving the properties of selenium through the use of alloy additions of arsenic as taught by the Ullrich and Mayer et al patents disclosed above, the advantageous properties imparted by the arsenic addition have been found useful and essential in certain types of xerographic imaging, such as rapid cycling in which multiple copies are made in a relatively short period of time. One characteristic of photoconductors in the arsenic-

selenium system, however, is that the addition of arsenic does result in an increased dark discharge over that exhibited by vitreous selenium. Although the dark discharge level for most arsenic-selenium alloys is not at a level to render it unsuitable for use in reusable xerography, the reduction or improvement of the dark discharge characteristic is a goal which would afford greater versatility with regard to use, and result in greater electrical efficiency because of the increased electrical potential available for development.

OBJECTS OF THE INVENTION

It is, therefore, an object of this invention to provide a method of reducing dark discharge in photoreceptors of the arsenic-selenium system.

It is a further object of this invention to provide a method of improving the electrical characteristics of arsenic-selenium photoconductive alloys.

It is yet another object of this invention to provide a xerographic plate which exhibits improved electrical characteristics.

It is a further object of this invention to provide a novel method of improving the electrical characteristics of an arsenic-selenium photoconductive layer.

BRIEF DESCRIPTION OF THE INVENTION

The foregoing objects and others are accomplished in accordance with this invention by providing a method of decreasing the dark discharge characteristics of photoconductors of the arsenic-selenium system by coating the photoconductor surface with a thin film of an organic material which is selected from the group consisting of a mixture of vinyl chloride and vinyl acetate, chloranil, the tributylamine salt of styrenemethacrylic acid, 2,4,7-trinitro-9-fluorene, p-benzoquinone, naphthylamine, hexachlorobenzene, polyvinyl carbazole, N-vinyl carbazole, N-N-dimethylallylamine, anthracene, aniline hydrochloride, mesitylene and phenoxy resins. By coating the photoconductor surface with a thin film of the organic materials noted above, surface charges which are contained on the photoconductor are prevented from injecting into the bulk of the photoconductor. This results in a significant decrease in the dark discharge characteristic of treated plates as compared to untreated plates. The resultant decrease in dark discharge of the coated arsenic-selenium photoconductor plate is further characterized by an increased electrical potential a short time after charging, and a decreased charging current which results in overall greater electrical efficiency.

DETAILED DESCRIPTION OF THE INVENTION

As stated above, suitable organic materials which have been found to be effective in decreasing the dark discharge of arsenic-selenium photoconductors when applied within a specific thickness range, include organic materials which are selected from the group consisting of a mixture of vinyl chloride and vinyl acetate, chloranil, the tributylamine salt of styrenemethacrylic acid, 2,4,7-trinitro-9-fluorene, p-benzoquinone, naphthylamine, hexachlorobenzene, polyvinyl carbazole, N-vinyl carbazole, N-N-dimethylallylamine, anthracene, aniline hydrochloride, mesitylene and phenoxy resins. By application of the organic material as a film having a thickness between about 25 to 2000 Angstrom Units over the surface of the photoconductor, acceptable reduction in dark discharge of the photoconductor

occurs without any adverse effects on the xerographic efficiency of the photoconductor.

It has been determined that the organic material must be in the form of a layer overlying the photoconductor with a thickness of between about 25 to 2,000 Angstrom Units to result in acceptable dark discharge rates with photoconductors of the arsenic-selenium type. If this layer or film thickness falls below about 25 Angstrom Units, no substantial reduction in dark discharge rate occurs, while if the layer thickness exceeds about 2,000 Angstrom Units then it becomes difficult to discharge the photoconductive layer upon exposure to illumination because of residual potential buildup across the coating which cannot easily be dissipated by an erase lamp. It should also be recognized in this regard, that the organic film or layer which is applied in the instant invention should not be confused with thicker organic overcoatings which are used primarily to protect photoconductive surfaces from abrasion, such as are illustrated by U.S. Pat. Nos. 2,860,048 and 3,146,145 to Deubner and Kinsella, respectively. Furthermore, the organic materials of the instant invention which comprise the coating should not be confused with photoconductor overcoatings of insulators such as hydrocarbons, or insulating resins such as polystyrenes which are also used to protect photoconductors, since these materials are not effective in reducing dark discharge rates of arsenic-selenium photoconductors.

The surface treatment of the arsenic-selenium alloy may comprise the application of the particular organic material in the form of a dilute solution of the material in any appropriate solvent. Typical solvents for the above organic materials include methyl isobutyl ketone, benzene, methyl alcohol, cyclohexane and isopropyl alcohol. In general, the organic material is diluted to a relatively weak solution in an appropriate solvent. Concentrations of from about 0.01 to 1.0 weight percent of the organic material have proven particularly satisfactory. Suitable techniques for applying the organic solution include dip or draw coating, swabbing the solution on the photoconductive surface by hand with absorbant cotton or cloth, applying with an applicator such as a squeegee, immersing for a few seconds in a bath of the solution, spraying or by rolling. Other means of applying the appropriate organic solution to the arsenic-selenium surface would occur to those versed in the art.

Arsenic-selenium alloys falling within the scope of the instant invention include arsenic in a concentration of about 0.5 to 50 percent by weight with the balance substantially selenium. The alloy is amorphous or vitreous in form and may be used in any conventional xerographic type application. U.S. Pat. Nos. 2,803,542 to Ullrich, 2,822,300 to Mayer et al and 3,312,548 to Straughan illustrate suitable arsenic-selenium alloys, methods of preparation, and the utility intended for the method and product of the instant invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples further specifically define the present invention with respect to a method of surface treating and testing an arsenic-selenium alloy layer. The examples and data below are intended to illustrate various preferred embodiments of the instant invention.

EXAMPLE I

A plate comprising a 40 micron layer of a 20 weight percent arsenic - 80 weight percent selenium alloy is formed by vacuum deposition on a polyethyleneimine interface contained on an aluminum substrate by the method set forth by Straughan in U.S. Pat. No. 3,312,548. The substrate is maintained at about 65°C during vacuum deposition with a vacuum of about 10^{-6} Torr. The final plate was sectioned into two parts designated sections "A" and "B," respectively, and rested in the dark overnight. Xerographic properties of the two sections were determined to be similar. The B section was then surface treated by dip coating with a 1 percent solution of N, N-dimethylallylamine in isopropyl alcohol. The plate was immersed in the coating bath for about one minute to form a dried coating thickness of several hundred Angstrom Units. The plates were again dark rested overnight (for about 18 hours) and retested the following day. Under identical charging conditions, the surface potential measured 1-½ seconds after charging was determined to be 220 volts for the untreated A section and 310 volts for the treated B section. This difference in surface potential is attributed to the reduced dark discharge of the treated plate.

EXAMPLE II

A second plate comprising a 40 micron layer of a 40 weight percent arsenic - 60 weight percent selenium alloy is deposited at 175°C on a chromic acid cleaned aluminum substrate using the method of Example I. The plate was then cut into sections designated A and B, and dark rested (for about 18 hours) overnight. The xerographic properties of the two sections were determined to be similar. The B section was then surface treated with a 1 percent solution of PKHH phenoxy polymer in 2-butoxyethanol (available from Union Carbide under the Tradename Bakelite PKHH). The plates were again dark rested overnight and retested the following day. The acceptance potential was determined to be 50 volts for the untreated A section and 95 volts for the treated B section. The charging conditions and results are similar to those of Example I.

EXAMPLE III

A series of 17 plates comprising a 40 weight percent arsenic - 60 weight percent selenium alloy were made by vacuum deposition to the following specification using the method set forth in Example I:

1. Eleven plates (Nos. 1-11) comprise a 40 micron layer of the arsenic-selenium alloy deposited on an aluminum substrate at about 180°-200°C.

2. Six plates (Nos. 12-17) comprise a 15 micron layer of arsenic-selenium alloy on a gold coated glass substrate at a deposition temperature of about 25°C.

The plates were first sectioned into two parts. One section of each plate was designated "Control" and not treated. The second section of each plate was treated with a 1 weight percent organic solution of the instant invention by dip-coating the section in an organic solution for about 1 to 2 minutes to form a dried coating about several hundred Angstroms thick on the surface of the arsenic-selenium photoconductor. The plates were rested in the dark overnight and were then electrically tested by first charging to a field of about 15 volts/micron of photoconductor thickness. The dark discharge was then determined in both the rested con-

dition and after cycling. The results of the testing are shown in Table I. The plates are numbered 1-17, with the untreated section designated "Control" and the treated section designated as such.

charged to a field of about 12 volts/micron of photoconductor thickness for plate 18-23 and about 8 volts/micron for plates 24-26. The dark discharge in 5 seconds was then determined for each plate.

TABLE I

SURFACE TREATMENT OF 40% As - 60% Se PHOTOCONDUCTOR			
PLATE NO.	TREATMENT	DARK RESTED * DARK DISCHARGE IN 5 SEC. (%)	CYCLED ** DARK DISCHARGE IN 5 SEC. (%)
1 (Control)	None	30	28
1 (Treated)	1% VYNS in methylisobutylketone (A mixture of 90% vinyl chloride and 10% vinyl acetate available from Union Carbide under the	5	15
2 (Control)	None	30	27
2 (Treated)	1% chloranil in methylisobutylketone	9	24
3 (Control)	None	28	39
3 (Treated)	1% tributylamine salt of styrene-methacrylic acid in benzene	18	33
4 (Control)	None	68	65
4 (Treated)	1% chloranil in methylisobutylketone	13	31
5 (Control)	None	100	100
5 (Treated)	1% 2,4,7-trinitro-9-fluorene in benzene	74	90
6 (Control)	None	100	86
6 (Treated)	1% p-benzoquinone in methyl alcohol	62	47
7 (Control)	None	43	49
7 (Treated)	1% naphthylamine in methyl alcohol	26	40
8 (Control)	None	97	76
8 (Treated)	1% hexachlorobenzene in benzene	65	69
9 (Control)	None	82	65
9 (Treated)	1% polyvinylcarbazole in cyclohexane	27	47
10 (Control)	None	50	83
10 (Treated)	1% polyvinylcarbazole in cyclohexane	6	20
11 (Control)	None	96	100
11 (Treated)	1% n-vinyl carbazole in benzene	50	81
12 (Control)	None	40	65
12 (Treated)	1% N,N-dimethylallylamine in isopropyl alcohol	17	23
13 (Control)	None	77	68
13 (Treated)	1% anthracene in benzene	44	54
14 (Control)	None	86	91
14 (Treated)	1% aniline-hydrochloride in methyl alcohol	56	62
15 (Control)	None	83	95
15 (Treated)	1% VYNS in methylisobutylketone	6	12
16 (Control)	None	60	82
16 (Treated)	1% N-vinylcarbazole in benzene	10	28
17 (Control)	None	65	86
17 (Treated)	1% mesitylene in methyl alcohol	45	39

* The dark discharge in the rested condition is determined by charging a given dark rested plate to the appropriate potential in the dark and measuring the voltage loss in 5 seconds with an electrometer probe. The ratio of the voltage lost in 5 seconds to the initial charged potential is the percentage of dark discharge.

** The cycled dark discharge is determined by charging a given dark rested plate to the appropriate potential in the dark followed by discharging the plate by exposure to a cool white fluorescent erase lamp. This cycle is repeated 20 times. The dark discharge is then determined as the ratio of the voltage loss in 5 seconds to the initial charged potential as set forth above.

EXAMPLE IV

A series of 9 additional plates are made by the method of Example I. These plates are number 18-26, respectively, and are made to the following specifications:

1. Plates 18, 19 and 20 comprise a 30 micron layer of a 0.5 weight percent arsenic — balance selenium layer deposited on an aluminum substrate held at 55°C during vacuum deposition.

2. Plates 21, 22 and 23 comprise a 30 micron layer of a 5 weight percent arsenic — balance selenium layer deposited on an aluminum substrate held at 55°C during vacuum deposition.

3. Plates 24, 25 and 26 comprise a 50 micron layer of a 16 weight percent arsenic — balance selenium layer deposited on an aluminum substrate held at 150°C during vacuum deposition.

One plate of each of the above three groups (Plates 18, 21 and 24, respectively) was designated a "Control" plate and was not treated by the process of the instant invention. The remaining plates were dip coating by the technique set forth in Example III to form an organic coating several hundred Angstroms thick on the surface of the arsenic-selenium photoconductive layer. All plates were dark rested overnight, and were

TABLE II

SURFACE TREATMENT OF 0.5, 5.0 AND 16.0% As - Se ALLOYS		
PLATE NO.	SURFACE TREATMENT	DARK RESTED DARK DIS- CHARGE IN 5 SEC. (%)
18 (Control)	None	14
19 (Treated)	1 wt% Polyvinyl Carbazole in methylene chloride	5
20 (Treated)	1 wt% PKHH Phenoxo Polymer in 2-butoxyethanol	3
21 (Control)	None	39
22 (Treated)	1 wt% Polyvinyl Carbazole in methylene chloride	6
23 (Treated)	1 wt% PKHH Phenoxo Polymer in 2-butoxyethanol	7
24 (Control)	None	33
25 (Treated)	1 wt% Polyvinyl Carbazole in methylene chloride	14
26 (Treated)	1 wt% PKHH Phenoxo Polymer in 2-butoxyethanol	10

The dark discharge is determined in the same manner as described for the values listed in Table I.

As shown by the examples, and the data contained in Tables I and II, the dark discharge of plates treated by

the process of the instant invention is markedly lower than that for the untreated plates. It can therefore be seen that the instant invention results in a method of significantly increasing the amount of surface voltage available for the development of photoconductors of the arsenic-selenium system.

Although specific components and proportions have been stated in the above description of the preferred embodiments of the instant invention, other suitable materials and procedures such as those listed above, may be used with similar results. In addition, other materials and changes may be utilized which synergize, enhance, or otherwise modify the instant invention. It should be understood that the organic coatings of the instant invention may be formed on the surface of the arsenic-selenium photoreceptor by a wide range of techniques other than those previously suggested. For example, the organic material may be incorporated as a component in the conventional cascade development process, or optionally, as a component in a liquid development system. It is also contemplated that the organic material may be simply applied in a separate intermediate step at some point in the conventional xerographic cycling of an arsenic-selenium drum.

Other modifications and ramifications of the present invention would appear to those skilled in the art upon reading the disclosure. These are intended to be within the scope of this invention.

What is claimed is:

1. A xerographic plate which consists essentially of a

supporting electrically conductive substrate, a photoconductive layer consisting essentially of an arsenic-selenium alloy having an arsenic content from about 0.5 to 50 percent by weight of said alloy overlaying said substrate, with said photoconductive layer being overcoated with an electrically insulating, thin film of a material selected from the group consisting of; a mixture of 90 weight percent vinyl chloride and 10 weight percent vinyl acetate, chloranil, the tributyl amine salt of styrenemethacrylic acid, 2,4,7-trinitro-9-fluorene, p-benzoquinone, naphthylamine, hexachlorobenzene, polyvinyl carbazole, N-vinyl carbazole, N-N-dimethylallylamine, anthracene, aniline hydrochloride, mesitylene, and phenoxy resins, said film having a thickness of between about 25 to 2,000 Angstrom Units.

2. The plate of claim 1 wherein said alloy has an arsenic content in an amount of about 40 percent by weight of said alloy.

3. The plate of claim 1 wherein said alloy has an arsenic content in an amount of about 20 percent by weight, of said alloy.

4. The plate of claim 1 wherein said alloy has an arsenic content in an amount of about 16 percent weight of said alloy.

5. The plate of claim 1 wherein said alloy has an arsenic content in an amount of about 0.5 percent by weight of said alloy.

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