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54 **Electrophotographic photoconductor.**

57 An electrophotographic photoconductor having a squaric acid methine dye charge generation layer - (CGL) which is coated onto an electrically conductive ground plane which exhibits electrical barrier layer properties, to thereby provide a photoconductor having improved dark decay and dark fatigue over a wide range of environmental conditions.

EP 0 220 489 A1

ELECTROPHOTOGRAPHIC PHOTOCONDUCTOR

Field of The Invention

The present invention relates to electrophotographic photoconductors, and in particular, to photoconductors having a squaric acid methine dye charge generating layer which is coated onto a metallic ground plane. The ground plane exhibits barrier layer properties.

Background of the Invention

The present invention relates to an improved xerographic photoconductor, and more specifically to the synergistic relationship which exists between only certain specific barrier layer ground plane members and a charge generation layer (CGL) which contains a squarylium compound.

The use of ground planes which exhibit barrier layer characteristics, and the use of a CGL which is based upon a squarylium molecule are individually known in the prior art. However, heretofore the use of the specific CGL and ground plane members defined herein, to form a xerographic photoconductor, was not known. Nor was it known that such a combination would solve problems such as dark decay and dark fatigue associated with a CGL which is based upon a squarylium molecule.

The prior art recognizes the advantages of using a barrier layer, i.e., an electrically insulating-like layer between the photoconductor's conductive metal ground plane and the CGL.

U.S. Patent 4,485,161 is exemplary. In this device, the barrier layer serves to reduce dark decay, i.e., charge leakage to the ground plane which occurs in the absence of light. This patent also recognizes the need for a barrier layer material which is not soluble in the solvents which are used to coat the CGL onto the barrier layer.

One of the barrier layers of the present invention is a polyamide barrier layer. Use of such a layer under the photoconductor's ground plane is taught by U.S. Patent 4,307,166.

U.S. Patent 4,495,263 is similar to the above-mentioned patent. In addition, this patent states that placing the polyamide barrier layer between the ground plane and the CGL is desirable since problems of haze, unstable sensitometry or unstable coatability result.

We have found that when the CGL is of a squarylium formulation, the problems mentioned by U.S. Patent 4,495,263 do not occur. In addition, use of a polyamide barrier layer with a squarylium-based CGL results in improved electrical perfor-

mance by reducing the effect that electrical conductivity coating defects have on the performance of the photoconductor in the xerographic process.

The present invention also teaches the use of specific aluminum alloys as the barrier layer type ground plane onto which the squarylium-based CGL is coated. U.S. Patent 4,461,820 is related in that it describes a photoconductor in which amorphous silicon is placed onto an aluminum oxide substrate. The use of aluminum alloys as a substrate is also suggested.

As noted above, the specific squarylium-based CGL of this invention is known in the prior art. The article entitled "Xerographic Photoconductor", in INTERNATIONAL TECHNOLOGY DISCLOSURES, Volume 1, N° 13, 25 November 1983, is exemplary. U.S. Patent 3,824,099 also describes squarylium dye molecules as photogenerating species in a photoconductor configuration.

The present invention is useful in making electrophotographic plates which have improved electrical response and improved useful electrical life.

The Invention

Electrophotographic photoconductors of the present invention comprise, in addition to an inert substrate, an electrically conductive ground plane of a critical construction and arrangement, and a CGL of a critical squarylium charge generating species.

A transport molecule may be used in a separate charge transport layer (CTL), or in conjunction with the CGL itself, to facilitate hole or electron mobility.

Such electrophotographic plates are extremely sensitive and have a panchromatic response which extends to 9000 Angstrom units. A particularly suitable field for their use is with solid state lasers emitting in the 7500 to 8500 Angstrom range.

There are several well known electrophotographic reproduction processes in current use. They differ in the particular way in which they are carried out, particularly in the sequence in which electric charging (usually with a corona) and illumination are carried out. All electrophotographic reproduction processes, however, involve the process step of selectively rendering portions of a photoconductor electrically conductive by selective exposure to light.

Photoconductivity involves at least two steps: 1) generation of charge; and 2) transportation of the charge. The present invention utilizes the ability of

squarylium dye species to efficiently generate electron-hole pairs upon absorption of light, giving rise to a latent electrostatic image, after the appropriate carriers are injected into the conductive ground plane and the transport molecule.

Initially, operation of such a photoconductor is very efficient, and the operation is consistent over a wide variety of environmental conditions. However, upon cycling, the photoconductor fatigues, that is, it no longer has the same sensitometric response as it did when it was new. As a result, the machine parameters must be adjusted to compensate for the changes, or the photoconductor must be replaced.

Some of the sensitometric responses that change as a result of cycling use are dark charge, residual potential, sensitivity and dark decay.

A particular problem with prior art squarylium-based photoconductors is that an increase in dark decay occurs at relative humidities of 15 % or less. This condition occurs after cycling the photoconductor, with exposure to light, in this environmental condition. This increase in dark decay varies as a function of the properties of the conductive ground plane, and this dark decay property can be very inconsistent, and can ultimately give poor print quality from machines which must perform in this environmental condition.

Prior art photoconductors which have been formulated using squarylium dyes as photogenerators, and using aluminum as the conductive ground plane, exhibit high variance with respect to this low humidity dark decay increase. This variance severely affects the manufacturing cost of the photoconductor as a result of the need for increased testing in order to assure high quality yield.

We have found that this dark decay effect, which normally occurs at low relative humidity as the photoconductor is cycled, is improved by combining specific conductive ground planes with a squarylium based CGL. By so doing, the undesirable dark decay increase which occurs upon cycling is alleviated to a great degree, and other sensitometric parameters of the photoconductor are also improved.

In those instances where the conductive ground plane is coated with a barrier-like material in accordance with the present invention, the coating must be insoluble in subsequent coating solvents which are used in fabricating the photoreceptor, particularly those which are used in coating the CGL onto the ground plane's coating. Since organic chemicals are usually used to fabricate photoconductors, it is very difficult to find barrier-like coating materials which are not affected to a great degree by these solvents. We have found several classes of polymers which exhibit this im-

pervious trait. Alcohol soluble polyamides are especially useful in the present invention, as are cross-linked epoxies and water-soluble polyvinyl alcohols (PVA).

We have also found that silicon dioxide, fabricated as an integral layer intermediate the CGL and aluminum ground plane, functions in a similar manner.

We have also found that certain alloys of aluminum, specifically silicon, calcium and gallium alloys, also function as ground planes in accordance with our invention.

Ground planes in accordance with our invention provide a relatively inexpensive and easy way to provide superior electrical properties to squarylium based photoconductors.

A further advantage of the present invention is that electrical defects caused by electron injection into the conductive ground plane are significantly reduced. Such defects can be caused by high work function contaminants which are present in or on the conductive substrate prior to the coating step. Injection from the CGL's generating specie, or from the CTL's transporting specie, is then very facile under applied field, and a dark decay defect will be present in the subsequent copy or print. Such contamination can be present as common dust which contains iron, a high function metal.

The following examples of the present invention are 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.

COMPARATIVE EXAMPLE 1 AND INVENTION EXAMPLE 1 (POLYAMIDE)

DuPont Poylester Type A, 300 gauge film was aluminized to an optical density of 1.7. This substrate was split into two sections, one for treatment in accordance with the present invention and the other to be processed as is.

The substrate to be treated was coated with a 0.1 micron layer of Elvamide 8061 (DuPont), a lower alcohol soluble co-polyamide of caprolactam hexamethyl adipamide and hexamethylene sebacamide. Methanol solvent was used. Both substrates were then coated with the following layers to fabricate a photoconductor:

1. An adhesive sublayer, about 0.1 micron thick, containing a mixture of Santolite MHP - (Monsanto) and PE-200, a polyester adhesive - (DuPont), in an equal weight ratio. Santolite is an aryl sulfonamide resin.

2. A squarylium generating layer, about 0.1 micron thick, containing a mixture of Santolite MHP and hydroxy squarylium in an 80/20 weight ratio. Coating solvents were pyrrolidine, morpholine and tetrahydrofuran.

3. A charge transport layer, about 20 microns thick, containing a mixture of 55 parts by weight Merlon M-60 polycarbonate resin (Mobay), 5 parts by weight PE-200 and 40 parts by weight the 1,1-diphenyl hydrazone of diethylamino benzaldehyde. The coating solvent was tetrahydrofuran.

The treated and untreated photoconductors - (Invention Example 1 and Comparative Example 1, respectively) were then tested in a sensitometer at less than 5% relative humidity. A charge corona was set to give an initial charge of negative 675 volts on the photoconductor. After 2000 cycles the dark voltage was measured, as was the dark decay rate. Dark fatigue is determined by subtracting the voltage on the photoconductor after 2000 cycles from the initial dark voltage as a function of time, and its units are volts per second. A quantity labeled as the total dark excursion (TDx) is the sum of the dark fatigue plus the dark decay rate. Low values of this sum are a measure of goodness. The TDx for the two films referenced are listed below:

1. Untreated Photoconductor: TDx = 180

2. Treated Photoconductor: TDx = 99

Prints made using these photoconductors, in a reproduction machine which uses a positive development system and which had cycled this many times at low humidity, would exhibit an optical density which was markedly lower when using the untreated photoconductor than when using the treated photoconductor of the present invention.

A photoconductor was then prepared as in this Example, except that the Elvamide layer was 0.05 microns thick and contained 35% by weight Santolite MHP in order to provide an improvement in adhesion to the aluminized substrate. The TDx was then monitored as a function of relative humidity. Each reading was calculated as described after 2000 cycles.

1. 3% Relative Humidity TDx 205

2. 4% Relative Humidity TDx 150

3. 9% Relative Humidity TDx 130

4. 15 % Relative Humidity TDx 110

5. 24 % Relative Humidity TDx 90

It can be seen that the concessions made to improve adhesion were deleterious to the beneficial effects of the all Elvamid layer.

COMPARATIVE EXAMPLE 2 AND INVENTION EXAMPLE 2 (Epoxy)

Aluminized Mylar (trademark) Type A was also used in these examples. Again one photoconductor

was prepared from an untreated aluminized substrate and the aluminum surface of the other was treated in the following manner in accordance with the present invention:

0.5 grams of Epon 1001 (Shell) was dissolved in 25 Milliliters of tetrahydrofuran. To this was added 1.5 milliliters of Versamid V-150 polyamide resin - (General Mills) at a 10% by weight loading in tetrahydrofuran. The resultant solution was coated onto the aluminum surface to a thickness of about 0.25 microns, and cured for two hours at 100°C. Epon is a brand name for a series of condensation products of epichlorohydrin and bisphenol A.

The two substrates were then coated with the following generating and transport layers to fabricate the photoreceptor.

1. The generating layer consisted of 1.5 grams of Epon 1009 (Shell) dissolved in 25 milliliters of tetrahydrofuran. To this solution was added a solution of 0.3 grams of hydroxy squarylium in 1 milliliter of ethylenediamine. This was then coated to a thickness of about one micron after the coating had cured for two hours at 100°C.

The TDx of the untreated film was 339 while that of the treated film was 71 when tested on a sensitometer which simulates the IBM 3800 laser printer. Both photoconductors were tested at a relative humidity of less than 10% and were cycled for four hours in order to identify these sensitometric differences.

INVENTION EXAMPLE 3 (PVA)

A photoconductor was prepared as in Invention Example 1, except that the coating used to treat the aluminized substrate was a polyvinyl alcohol - (PVA) solution in water (Aldrich Chemical Co.). When tested in the sensitometer as described in Example 1, the total dark excursion of this sample was 147. This represents an improvement of 33 over the control photoconductor whose aluminum substrate was untreated, and gave a TDx of 180.

COMPARATIVE EXAMPLE 4 AND INVENTION EXAMPLE 4 (Alloys of Aluminum)

Type A Mylar film was aluminized with pure aluminum, to form a comparative example, and then films were metallized with the following alloys to form three examples of the present invention (I, II, and III), and a comparative example (IV): O-AlCa (95:5); II-AISi (95:5); III-AlGa (95:5); IV-AISn (95:5). Photoconductors were prepared as in Example 1, and the TDx was determined as in Example 2.

1. Comparative Example TDx 266

- 2. I TDx 102
- 3. II TDx 140
- 4. III TDx 160
- 5. IV TDx 373

From this data it is clear that the alloys of aluminum I, II and III alleviate the low humidity total dark excursion.

COMPARATIVE EXAMPLE 5 AND INVENTION EXAMPLE 5 (Silicon Dioxide)

Aluminized Mylar Type A film was used as described in Example 1. Half of this substrate was treated by e-beam evaporating a 30 Angstrom thick layer of silicon dioxide on top of the aluminum. The photoconductor fabricated in Example 1 was then coated on the untreated and treated aluminized Mylar. When tested as described in Example 1, the TDx values were as follows:

- 1. Untreated: TDx 193
- 2. Treated: TDx 106

While our invention has been particularly shown and described with reference to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the spirit and scope of the invention.

Claims

1. An electrophotographic photoconductor, comprising:

a light sensitive layer containing squaric acid methine dye coated onto a conductive ground plane layer, the ground plane being selected from one of the following:

an impervious organic polymeric layer intermediate

said dye layer and a metallic conductive layer, to separate the generating specie from the conductive layer;

an aluminum alloy selected from one of AlCa, AlSi or AlGa;

a silicone dioxide layer intermediate said dye layer and a metallic conductive layer, to separate the generating specie from the conductive layer.

2. The photoconductor defined by Claim 1 wherein the organic layer is a polyamide.

3. The photoconductor defined by Claim 2 wherein the polyamide is a lower alcohol soluble co-polyamide of caprolactam, hexamethylene adipamide and hexamethylene sebacamide.

4. The photoconductor defined by Claim 1 wherein the organic layer is an epoxy resin.

5. The photoconductor defined by Claim 4 wherein the epoxy is of the bisphenol A type.

6. The photoconductor defined by Claim 1 wherein the organic layer is a polyvinyl alcohol polymer.

7. A photoconductor defined by Claim 1 wherein the squaric acid methine dye layer is a charge generation layer, and including a charge transport overcoat layer.

8. A photoconductor defined by Claim 1 wherein the squaric acid methine dye is present in an inert binder.

9. A photoconductor defined by Claim 1 wherein the squaric acid methine dye is present in a single layer containing a charge transport specie.

10. A photoconductor defined by Claim 7 wherein the conductive ground plane is aluminum, the squaric acid methine dye is 2-4 bis (2-hydroxy-4-dimethyl aminophenyl) 1-3 cyclobutene diylum 1-3 diolate, and the transport layer includes the transport molecule 1,1 diphenyl hydrazone of diethylaminobenzaldehyde.

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DOCUMENTS CONSIDERED TO BE RELEVANT			EP 86113052.4
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	<u>US - A - 4 471 041 (BARANYI)</u> * Claims 1,2,5-12,19,20; column 11, lines 9-19; column 13, lines 43-52 * --	1-10	G 03 G 5/10 G 03 G 5/09 G 03 G 5/14 G 03 G 5/06
X	<u>US - A - 4 391 888 (CHANG)</u> * claims 1,4,8 * --	1,7-10	
X	<u>EP - A1 - 0 102 850 (XEROX)</u> * Claims 1-3,6 * --	1,7-10	
D,Y	<u>US - A - 4 495 263 (VANDERVALK)</u> * Claims 1,2,7 * --	1-3	
A	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 24, no. 11 B , April 1982, New York, USA R.D.BALANSON et al. "Reduction of fatigue in squarylium particulate photoconductor by electrontrans- port doping" page 6194 * Lines 4-8,24 * --	1,7-10	TECHNICAL FIELDS SEARCHED (Int. Cl.4) G 03 G C 09 B
D,A	<u>US - A - 4 461 820 (SHIRAI)</u> * Column 4, lines 50-55 * -----	1	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 26-01-1987	Examiner SCHÄFER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			