

[54] PHOTOCONDUCTOR OVERCOATED WITH TRIARYLPYRAZOLINE CHARGE TRANSPORT LAYER

3,549,362 12/1970 Carpenter et al. 96/1.6
 3,598,582 8/1971 Herrick et al. 96/1.5
 3,684,548 8/1972 Contois 96/1.6 X

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FOREIGN PATENTS OR APPLICATIONS
 4,326,710 11/1968 Japan 96/1.6
 1,030,024 5/1966 Great Britain 96/1.5

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[21] Appl. No.: 323,677

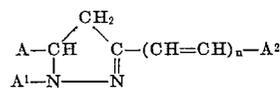
[57] ABSTRACT

Electrophotographic plates are provided having a charge generation layer and a separate charge transport layer comprising a tri-aryl pyrazoline compound having the formula:

[52] U.S. Cl. 96/1.5, 96/1.6, 252/501, 117/215, 117/218

[51] Int. Cl. G03g 5/04, G03g 5/06, G03g 5/08

[58] Field of Search 96/1 PE, 1.5, 1.6, 1 R; 252/501



[56] References Cited

UNITED STATES PATENTS

3,180,729 4/1965 Klupfel et al. 96/1.5
 3,384,488 5/1968 Tulagin 96/1 PE
 3,527,602 9/1970 Fox et al. 96/1.5 X
 3,535,221 10/1970 Tulagin 96/1 PE

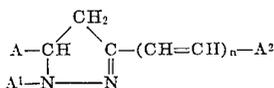
wherein n is zero or one, and A, A¹ and A² are each aryl radicals.

4 Claims, No Drawings

PHOTOCONDUCTOR OVERCOATED WITH TRIARYLPYRAZOLINE CHARGE TRANSPORT LAYER

FIELD OF THE INVENTION

The present invention is concerned with layered electrophotographic plates. In particular it is concerned with electrophotographic plates having a charge generating layer and a separate charge transporting layer. According to the present invention, the charge transporting layer always comprises at least one tri-aryl pyrazoline compound having the formula:



wherein n is zero or one, and A, A¹ and A² are each aryl radicals.

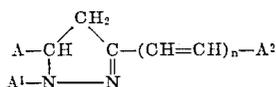
PRIOR ART

The pyrazoline compounds useful in the present invention are known materials and their preparation has been described in the literature. The prior art teaches that such materials are known to be photoconductors. The photoconductive nature of pyrazolines is taught in U.S. Pat. Nos. 3,180,729 and 3,549,362.

SUMMARY OF THE INVENTION

It has now been found that electrophotographic plates having unexpected advantages can be prepared using certain pyrazoline compounds in a charge transport layer which is used in conjunction with a separate charge generating layer.

the pyrazoline compounds useful in the present invention are those having the formula



wherein n is zero or one, and A, A¹ and A² are each aryl radicals.

In this formula it is preferred that $n = 1$, in which case the materials may be classified chemically as styryl pyrazolines. It is also preferred that one or more of the aryl groups be substituted, most preferably with groups known in the art to be electron donating groups. The most preferred substituent groups are methoxy, ethoxy, dimethyl amino, diethyl amino and the like. It is not preferred to substitute the aryl groups with electron withdrawing groups such as nitro and cyano.

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. The charge transport layers of the present invention are useful in making electrophotographic plates useful in all such processes.

It is one of the unexpected advantages of the present invention that the charge transport layers may be used with any of a wide variety of separate charge generating layers. For example, the charge generating layer may be selenium or an alloy of selenium. It may be other inorganic materials such as compounds from groups II and VI of the periodic table, for example cadmium sulfide-selenide. Alternatively, the charge generating material may be an organic material, for example a cyanine compound such as those shown in U.S. Pat. application Ser. No. 129,637, a disazo compound such as those shown in U.S. Pat. application Ser. No. 129,635, now abandoned, or a phthalocyanine compound. Particularly outstanding results have been obtained when the charge generating layer comprises a compound which is a methine dye derived from squaric acid. Materials of this type are discussed in U.S. Pat. application Ser. No. 323,678 filed on even date herewith.

The charge transport layers of the present invention may be used either on top of the charge generating layer, or beneath the charge generating layer. For mechanical reasons, it is generally preferred that the charge transport layer be on top. The charge transport layer may vary considerably in thickness, in general being from about 10 to about 30 microns thick, preferably from about 15 to about 25. When the charge transport layer is on top of the charge generating layer, i.e. when the charge generating layer is between the charge transport layer and the conductive substrate, the electrophotographic plate should be charged negatively. In those instances where the charge transport layer is beneath the charge generating layer, that is, when the charge transport layer is between the charge generating layer and the conductive substrate, the electrophotographic plate should be charged positively. The theoretical explanation for this is not known with certainty. It is theorized that the pyrazoline charge transport layers of the present invention operate by transporting holes, and this explanation would be consistent with those data.

Photoconductivity involves at least two steps: (1) the generation of charge, and (2) the transportation of charge. The present invention utilizes the ability of the pyrazoline containing layer to transport the charge generated in the separate charge generating layer. Among the unexpected advantages of the present invention, it should be particularly mentioned that the pyrazoline containing materials have the unexpected ability not only to transport the charge, but also to accept injection of the charge, that is, to allow the charge to cross the interface between the separate charge generating layer and the charge transport layer. This is true with both organic and inorganic charge generation layers.

The pyrazoline compounds of the present invention have the additional advantage of being film forming. They may, therefore, be used by themselves to form the charge transport layer. For mechanical reasons, however, it is generally preferred to use them in conjunction with a binder. In most instances it is preferred to use roughly from about 1 part to about 3 parts by weight binder to one part by weight pyrazoline. Many types of binder materials such as resins are known to the prior art. Particularly good results have been obtained using polyester resins and polycarbonates. Polyvinylidene chloride and polystyrene may also be used, as may acrylic resins of low molecular weight.

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 1

A charge generating layer consisting of 68% Se, 30% Te, and 2% As (weight percent) evaporated on a conductive substrate which was dip coated with a barrier layer with a dry thickness of approximately 0.3 microns. The barrier layer was coated with a solution of 3 parts polyester (Goodyear VPE 200) and 1 part 1-phenyl-3-[p-dimethylaminostyryl]-5-[p-dimethylaminophenyl]-pyrazoline which had been dissolved in tetrahydrofuran. Method of coating was knife blade with a wet gap setting of 5 mils. The composite layer was heated 16 hours at 55° C with a resulting dry thickness of 15 microns.

The photoconductor was corona charged in the dark to a negative voltage of approximately 700 volts. The sample was then exposed to a light source of a photocopy green lamp. The initial dark charge was reduced to 200 V with an exposure of 0.33 micro joules/cm².

EXAMPLE 2

A solution prepared from tetrahydrofuran and consisting of 3 parts of polyester and 1 part pyrazoline (as in Example No. 1) was knife blade coated at a wet thickness of 5 mils on a conductive substrate. The layer was dried for 2 hours at approximately 80° C to remove excess solvent. Dry thickness was approximately 12 microns. The photoconductor was charged on a rotating disc electrometer to a negative voltage of 600 volts. Exposure to a tungsten source reduced the dark charge to 500 Volts (approximately 20 percent decay) after 4.0 seconds. By comparison, the layered photoconductor from Example No. 1 was dark charged on the rotating disc electrometer to a negative voltage of 880 V and exposed to the tungsten source plus a 1.47 neutral density filter plus opal glass. The original dark charge of -880 was reduced 20 percent after 0.15 sec. (70X increase) and to a 200 volt level in 0.7 seconds.

EXAMPLE 3

Approximately 1 gram of a cyanine dye, 3-ethyl-2-[5-(3-ethyl-2-benzothiazolynylidene)-1,3-pentadienyl] benzothiazolium iodide was placed in a McCrone micronizing mill (a vibro-energy laboratory mill available from McCrone Research Associates, London, England) and was ground as a dry powder for 60 minutes. Approximately 10 grams of tetrahydrofuran and 0.15g of a polyvinylbutyral resin - Vinylite XYHL (available from Union Carbide and Carbon Company) was added to the powder and was ground for an additional 30 minutes. The resultant slurry was reduced in concentration by additional tetrahydrofuran and was applied to an aluminized Mylar substrate using a meniscus coater. (Mylar is duPont's brand of polyethyleneterephthalate.) The thin dye layer (less than 2 microns) was then dip coated with a solution containing 1 part 1-phenyl-3-[p-diethylaminostyryl]-5-[p-diethylaminophenyl]-pyrazoline, 1.5 parts Merlon 60 (a polycarbonate resin available from Mobay Chemical Company) and 16 parts tetrahydrofuran. The thickness of the layer was approximately 17 microns.

The photoconductive plate was corona charged in the dark to a negative voltage of approximately 700

volts. The sample was exposed to a tungsten light source filtered with wavelength filters to give maximum intensity at approximately 5,500 angstroms. The initial dark voltage of 700 volts was reduced to 200 volts by an exposure of approximately 0.7 micro joules/cm².

EXAMPLE 4

A selenium alloy charge generating layer was prepared in the same manner as Example No. 1. The layer was dip coated with a solution of one part polyester and one part 1-phenyl-3-[p-methoxystyryl]-5-[p-methoxyphenyl]-pyrazoline dissolved in tetrahydrofuran. The coating was dried for 40 hours at 55° C to remove excess solvent with a resulting dry thickness of 16 to 18 microns.

The photoconductive plate was negatively charged in the dark to approximately 700 volts. The plate was then exposed to a photocopy green lamp. The initial dark charge was reduced to 200 volts with an exposure of 0.32 micro joules/cm².

EXAMPLE 5

A selenium alloy charge generating layer was prepared in the same manner as Example No. 1. The layer was dip coated with a solution of two parts polyester and one part 1-phenyl-3-[p-diethylaminostyryl]-5-[p-diethylaminophenyl]-pyrazoline dissolved in tetrahydrofuran. The coating was dried for 72 hours at 60° C to remove excess solvent with a resulting dry thickness of 15 microns.

The photoconductor was corona charged in the dark to a negative charge of 700 volts and then was exposed to a photo-copy green lamp. The initial dark charge was reduced to 200 volts with an exposure of 0.24 micro joules/cm².

EXAMPLE 6

A charge generating layer consisting of a Se alloy was evaporated directly onto a conductive substrate. A charge transport layer was formulated and coated in the same manner as Example No. 5.

The photoconductor was corona charged in the dark to a negative voltage of approximately 600 volts. The plate was then exposed to a photocopy green light source and the dark charge reduced to 200 volts with an exposure of 0.24 micro joules/cm².

EXAMPLE 7

A charge generating layer consisting of Cd S Se approximately 0.3 microns thick was coated on a conductive substrate by a chemical vapor deposition technique. A charge transport layer consisting of 3 parts polyester and one part 1-phenyl-3-[p-dimethylaminostyryl]-5-[p-dimethylamino phenyl]-pyrazoline was knife coated to a dry thickness of approximately six microns.

The photoconductor was dark charged on a rotating disc electrometer to a negative charge of 390 volts. The sample was exposed to a tungsten source with the initial dark charge being reduced to 200 volts in 0.15 sec.

EXAMPLE 8

A charge transport layer consisting of two parts polyester and one part 1-phenyl-3-[p-diethylaminostyryl]-5-[p-diethylamino phenyl]-pyrazoline was dissolved in a suitable solvent. The solution was dip coated in a conductive substrate and dried to an approximate thick-

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ness of 15 microns. A charge generating layer consisting of 2-p-dimethylaminostyrylquinoline ethiodide dye was rubbed onto the surface of the transport layer (thickness, less than 2 microns).

The photoconductor was then positively charged on a rotating disk electrometer to a dark charge of 720 volts. The initial dark charge was decayed with a tungsten lamp to 200 volts in 0.80 seconds.

EXAMPLE 9

A second charge transport layer prepared in the same manner as in Example No. 7 was coated with a thin dye layer of pyrazlone red.

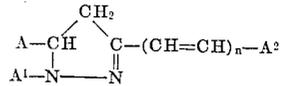
The photoconductor was positively charged to a dark voltage of 920 volts on the rotating disc electrometer. The initial dark voltage was then reduced with a tungsten exposure source to 200 volts in 0.70 seconds.

What is claimed is:

1. An electrophotographic process comprising the steps of negatively charging and image-wise exposing to light an electrophotographic plate comprising a conductive substrate, a layer comprising a photoconductor selected from the group consisting of selenium and its alloys, compounds of an element from Group II and an

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element from Group VI of the periodic table, cyanine compounds, disazo compounds, and phthalocyanine compounds, and, overcoating said layer of photoconductor, a separate layer from 10 to 30 microns thick comprising a compound having the formula:



wherein n is zero or one, and each of A, A¹ and A² is a phenyl group or a phenyl group substituted with an electron donating group.

2. A process as claimed in claim 1 wherein n is one.

3. A process as claimed in claim 1 wherein the overcoat layer comprises a resin binder.

4. A process as claimed in claim 1 wherein the overcoating layer comprises the compound 1-phenyl-3-[p-diethylaminostyryl]-5-[p-diethylamino phenyl]-pyrazoline.

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