

tacted with the layer containing the latent image whereby the powder is attracted to the charged portions of the layer and repelled by the uncharged areas, thereby resulting in a visible image.

The electroscopic powder ordinarily consists of a carrier material and a toner. The carriers may comprise tiny glass beads, iron powder, tiny plastic balls, etc. The toner may consist of a pigmented polymeric powder, such as a resin-carbon black mixture.

Optionally, the developer may comprise a solution of a resin or pigment and a liquid which is similarly attracted to the charged portions of the exposed layer. Following development, the image may be fixed according to any of the known methods. For example, the developed image may be heated or may be transferred to another support material prior to fixing.

Rather than first charging the photoconductive layer prior to exposure, an episcopic or diascopic image may be projected thereon employing any of the projecting apparatus known in the prior art, followed by electrostatic charging. The resulting electrostatic image is then developed and fixed as described above.

Optionally, employing a dual charging technique, an electrophotographic material wherein the support layer is nonconductive may be employed. This method is described in detail in U.S. Pat. No. 2,922,883, Jan. 26, 1960 to Giaimo. Briefly, the electrophotographic element to be charged is passed between two corona discharge devices. One of the corona devices produces a negative corona, bombarding one surface of the member with negative ions. The other device bombards the opposite surface with positive ions. This system produces opposite charges on opposing sides of the element, thereby eliminating the necessity for a conductive backing. Obviously, this method would also be applicable where no supporting substrate was employed. Thus, the invention also contemplates unsupported photoconductive insulating layers.

It has been unexpectedly found, however, that the photoconductive materials of the present invention give unusually good results when utilized in the so-called "persistent mode" electrophotographic process. This process is described in detail in U.S. Pat. No. 2,845,348, July 29, 1958 to Kallmann.

Briefly, the method comprises exposing the electrophotographic element to a light pattern which produces a corresponding latent image of conductivity in the element. This conductivity image pattern will persist for an extended period of time as long as the element is shielded from light. This latent image is developed by charging the element with electricity, thereby forming an electrostatic image which corresponds to the conductivity image. The electrostatic image may then be further developed according to any of the above-described methods, such as by cascading thereover pigmented toner particles.

It has been unexpectedly found that the photoconductive materials of the present invention give especially advantageous results when employed according to the above-described process. A similar method is also described in the copending application Ser. No. 474,583 to C. E. Herrick et al., filed July 26, 1965.

Still another method comprises charging the photoconductive layer and exposing the same simultaneously through transparent electrodes. The resulting image may be developed and fixed by any of the procedures described above.

The final, fixed electrophotographic images may be utilized according to any of the techniques known in the art. For example, the image may be converted into printing plates, employed as masters for the production of additional copies, etc.

The invention is further illustrated by the following nonlimiting examples.

EXAMPLE 1

1,3-diethyl-5[5-(2,3,6,7-tetrahydro-(1H, 5H)-benzo-

(i,

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j)-quinolizin-9-yl) - 1,3-neopentylene - 2,4 - pentadienylidene]-2-thiobarbituric acid (0.25 gram) was dissolved in 5 ml. of dichloroethane and added to 1 gram of a 25% polystyrene solution. This solution was coated on an aluminum plate using a 5 mil wet gap. The resulting assembly was dried to yield an electrophotographic film having a thickness of 7-8 μ .

The resulting electrophotographic material was tested for its electrophotographic speed utilizing a rotating disc electrometer, frequently employed for the study of photoelectric decay of photoconductors. The unit consists of a motor driven disc at 3600 r.p.m. on which a sample holder is mounted. The sample size is $\frac{1}{2}$ inch in diameter. The charging station consists of a double wire corotron on which the voltage can be varied from 4 to 8 kv., and the polarity can be changed either to positive or negative. The next station on the path of the sample and 180° away is the detector or probe. This consists of a copper tip micrometer (to adjust distance to sample) which is insulated to ground and attached across a dropping resistor to an oscilloscope. As the moving charge sample moves by the probe, a current is induced in the probe which is read as voltage across the resistor on an oscilloscope. The last station is an exposure port with an electronic shutter through which a tungsten projection lamp can be flashed. In the actual testing of a sample disc, the corotron is turned on and the sample is allowed to pass under it for as many times as necessary for it to attain equilibrium charge. Then it rotates past the transparent probe where the signal is monitored and the sample exposed, the decay of the charge on the sample is monitored by the oscilloscope.

The electrophotographic, photoconductive film was found to have an electrophotographic speed 20 times less than that of selenium.

EXAMPLE 2

The above-described procedure was followed with the exception that 10 milligrams of the activator 2,2',4,4',6,6'-hexanitrodiphenylamine was added to the polymeric solution prior to coating on the aluminum plate.

The resulting assembly was found to have an electrophotographic speed equal to that of selenium.

EXAMPLE 3

The procedure of Example 2 was followed with the exception that the photoconductor used was 1,3-diethyl-5[p-dimethylaminophenyl - 1,3-neopentylene - 2,4-pentadienylidene]-2-thiobarbituric acid. The resulting plate was found to have an electrophotographic speed 3 times less than that of selenium.

EXAMPLE 4

The procedure of Example 2 was followed with the exception that the photoconductor employed was 1,3-diethyl - 5[p - dimethylaminophenyl - 1,3-neopentylene-2,4-pentadienylidene] - 2 - thiobarbituric acid. The resulting plate was found to have an electrophotographic speed 3 times less than selenium.

EXAMPLE 5

The procedure of Example 1 was followed with the exception that the activator employed was 3,5-dinitrobenzoic acid. The resulting photographic plate showed a speed 3 times less than selenium.

EXAMPLE 6

The procedure of Example 1 was followed with the exception that the activator employed was tetrabromophthalic anhydride. The resulting plate showed a speed 4 times slower than selenium.

EXAMPLE 7

The procedure of Example 1 was followed with the exception that the photoconductor was activated with 2,6-diphenol-p-benzoquinone. The resulting plate showed

a speed 4 times slower than selenium when tested by the method of Example 1.

EXAMPLE 8

A solution containing 3 grams of 7% polyvinylcarbazole in dichloroethane, 0.2 gram of 1,3-diethyl-5-[5-(2,3,6,7-tetrahydro-(1H,5H)-benzo-(i,j)-quinolizin-9-yl)-1,3-neopentylene-2,4-pentadienylidene]-2-thiobarbituric acid and 10 milligrams of hexanitrodiphenylamine was coated on an aluminum plate using a 7 mil wet gap and dried resulting in an electrophotographic, photoconductive film having a thickness of 7μ .

The procedure of Example 1 was followed to test the electrophotographic speed of the resulting material. The material was found to have a speed twice that of selenium.

EXAMPLE 9

A solution of 0.25 gram of polyvinylbenzofuran, 0.25 gram of [5-2,3,6,7-tetrahydro - 1H,5H - benzo-i,j]-quinolizin-9-yl] - 1,3 - neopentylene-2,4-pentadienylidene]-malonitrile and 20 milligrams of hexanitrodiphenylamine and 4 ml. of dichloroethane was coated on an aluminum plate, using a 7 mil wet gap giving a resulting dried film having a thickness of $7-8\mu$. The material was tested according to the procedure in Example 1 and found to have selenium speed.

EXAMPLE 10

A mixture containing 0.25 gram of the photoconductor of Example 9 and 10 milligrams of hexanitrodiphenylamine and 1 gram of a 25% polystyrene solution in dichloroethane was coated on an aluminum plate using a 5 mil wet gap. The resulting photoconductive film had a thickness of $7-8\mu$ and showed a speed one-half that of selenium when tested in accordance with the method described in Example 1.

The following example illustrates the above-described "persistent mode" electrophotographic process employing the photoconductors of the invention.

EXAMPLE 11

A film prepared according to the procedure of Example 2 gave an image, when exposed for 2 seconds to a 40 watt tungsten lamp at 12 inches through a positive transparency, and then corona charged at 6 kv.

The resulting image was toned with Xerox 914 toner 45 using the cascade method. The thus developed image was fixed by heating.

EXAMPLE 12

A formulation comprising 0.25 gram of 1,3-diethyl-5-[5-(2,3,6,7-tetrahydro - (1H,5H) - benzo - (i,j)-quinolizin-9-yl)-1,3-neopentylene - 2,4 - pentadienylidene]-2-thiobarbituric acid (0.25 gram) and 1.0 gram of a 25% polystyrene solution in 5 ml. of dichloroethane was coated on an aluminum slide using a 5 mil wet gap. The sample was charged positively with a Model D Xerox Processor set at 7 kv. The exposure conditions were 0.1 second using a 40 watt tungsten bulb at 20 inches through a positive transparency. The images were toned with Xerox 914 toner using a cascade method and transferred to paper. The image quality had good density without any background.

EXAMPLE 13

The procedure of Example 12 was followed except that .01 gram of 2,2',4,4',6,6'-hexanitrodiphenylamine was added to the formulation prior to coating. The exposure conditions were 0.1 second at 30 inches using a 15 watt tungsten bulb. The copy had good image density, good contrast and no background.

EXAMPLE 14

A formulation comprising 0.2 gram of 1,3-diethyl-5-[p-diethylaminophenyl]-1,3-neopentylene - 2,4 - pentadienylidene]-2-thiobarbituric acid, 1.0 gram of 25% styrene solution and 5 ml. of dichloroethane was coated on an 75

aluminum slide using a 5 ml. wet gap. The procedure of Example 12 was followed employing exposure conditions of 0.1 second at 30 inches using a 40 watt tungsten bulb. The copy had good image density without any background.

EXAMPLE 15

The procedure of Example 14 was followed except that .01 gram of hexanitrodiphenylamine was added to the formulation and exposure conditions of 0.1 second at 30 inches using a 15 watt tungsten bulb were employed. The image quality had no background and good image density.

EXAMPLE 16

A formulation of 0.25 gram of 1,3-diethyl-5-[p-diethylaminophenyl] - 1,3-neopentylene-2,4-pentadienylidene]-2-thiobarbituric acid, 1.0 gram of a 25% polystyrene solution and 5 ml. of dichloroethane was coated on a aluminum plate using a 5 mil wet gap. The procedure of Example 12 was followed employing exposure conditions of 0.5 second at 30 inches using a 15 watt bulb. The copy was free of background and had excellent image density.

EXAMPLE 17

The procedure of Example 12 was followed except that .01 gram of 3,5-dinitrobenzoic acid was added to the formulation. The exposure conditions were 0.2 second at 30 inches using a 15 watt bulb. The copy had good image density and no background.

EXAMPLE 18

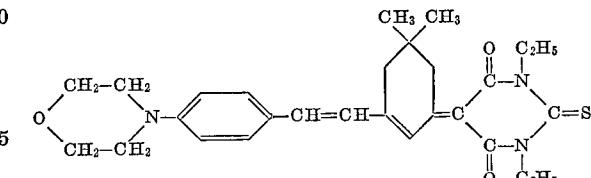
The procedure of Example 5 was followed except that .013 gram of 2,6-diphenyl-p-benzoquinone was added to the formulation. The exposure conditions were 0.3 second at 30 inches using a 15 watt bulb. The copy had no background and good image density.

EXAMPLE 19

A formulation of 0.25 gram of [5-2,3,6,7-tetrahydro-1H,5H - benzo - i,j] - quinolizin-9-yl]-1,3-neopentylene-2,4-pentadienylidene] - malonitrile, (X=a; Y=b), 1.0 gram of a 25% polystyrene solution and 2.5 ml. of dichloroethane was coated on an aluminum slide using a 5 mil wet gap. The exposure conditions were 1½ seconds at 30 inches with a 15 watt tungsten bulb. The image had essentially no background and good image density.

EXAMPLE 20

A formulation of 0.12 gram of



60 0.005 gram of hexanitrodiphenylamine, 0.1 gram of polyvinylformal, and 1 ml. of dichloroethane was coated on an aluminum slide with a doctor blade set at a 5 mil wet gap. The procedure of Example 12 was followed using exposure conditions of 2.0 seconds at 30 inches with a 15 watt bulb. The copy produced had no background and good image density.

EXAMPLE 21

The formulation of Example 1 was used except that 0.015 gram of tetrabromophthalic anhydride was added to the formulation. The exposure conditions were 0.1 second at 30 inches with a 15 watt bulb. The copy produced had good image density and no background.

The following examples illustrate the invention wherein the above-described photoconductors are used as sensitizing dyes for other photoconductor substances.

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3,536,484

SMALL MOLECULE HETEROCYCLIC PHOTOCONDUCTORS AND THEIR USE IN ELECTROPHOTOGRAPHY

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U.S. Cl. 96—1.5

18 Claims

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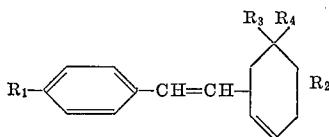
heterocyclic compounds have been employed as photoconductive materials. These prior art photoconductive materials suffer from many disadvantages, however. Many known photoconductors show low sensitivity when used alone and require sensitization with various dyestuffs and/or activators. These additives often increase the electrophotographic speed of the systems in which they are employed; however, many of the dyestuffs conventionally employed lack stability and result in dye fading, etc. Moreover, the low solubility of the prior art photoconductors, dyestuffs and activators and organic solvents is quite low, thereby limiting the quantity of the material which can be coated onto electrophotographic supports for use in these systems.

It is an object of the present invention to provide an electrophotographic, photoconductive material free from the disadvantages of the prior art.

It is a further object of the present invention to provide a novel electrophotographic reproduction process.

20 **BRIEF DESCRIPTION OF THE INVENTION**

Briefly, the present invention relates to a novel electrophotographic, photoconductive material comprising a support layer and a photoconductive insulating layer containing a photoconductor having the formula:



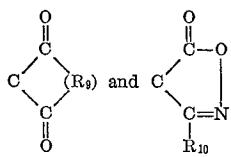
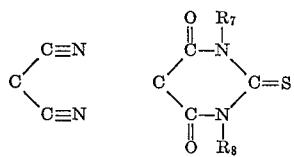
wherein:



R₁ is selected from the group consisting of:

morpholino, thiomorpholino, piperidino and julolidinyl;

R₂ is selected from the group consisting of:



R₃, R₄, R₅, R₆, R₇ and R₈ may be the same or different and are lower alkyl groups.

R₉ is the residue of a one, two or three fused ring aryl group such that the ring is a five membered ring with C₆H₄ being preferred.

R₁₀ is selected from the group consisting of aryl and substituted aryl groups with phenyl being the most preferred.

The invention also includes a reproduction process comprising forming an electrostatic charge pattern on these materials and developing the image.

BACKGROUND OF THE INVENTION

Electrophotographic reproduction processes generally comprise forming an electrostatic charge pattern on a photoconductive material and then developing the pattern, usually by contact with an electroscopic powder. These processes depend on the phenomena that certain photoconductive substances are capable of holding an electrostatic charge in the absence of light; however, the charge is dissipated upon exposure of the photoconductive material to light.

In the past, various inorganic substances, such as selenium, sulphur and zinc oxide and organic compounds, such as anthracene, anthraquinone, benzidine or various

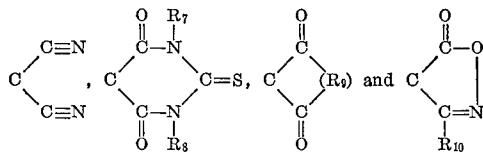
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R₁ is selected from the group consisting of



morpholino, thiomorpholino, piperidino and julolidinyl;

R₂ is selected from the group consisting of:



R₃, R₄, R₅, R₆, R₇ and R₈ may be the same or different and are lower alkyl groups.

R₉ is the residue of a one, two or three fused ring aryl group such that the ring is a five membered ring with C₆H₄ being preferred.

R₁₀ is selected from the group consisting of aryl and substituted aryl groups with phenyl being the most preferred.

The invention also provides a novel electrophotographic reproduction process comprising forming an electrostatic charge pattern on photoconductive materials containing the above-described photoconductors and developing the image.

The novel photoconductors of the present invention possess several highly advantageous and desirable properties. They have been found to exhibit a high order of electrophotographic speed. When activated with many of the known activators, the electrophotographic speed of these photoconductors is increased to within the range of selenium, a commercially employed inorganic photoconductor. Moreover, the photoconductors of the present invention are highly colored, thereby eliminating the need for the addition of sensitizing dyes. In addition, because they are highly colored, these materials may also be em-

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ployed as sensitizing dyes for other photoconductive materials. Inasmuch as many of the known sensitizing dyes are highly unstable, it is a distinct advantage of the present invention that their presence in the electrophotographic material is unnecessary. In addition, the photoconductors of the present invention are highly soluble in a wide range of organic solvents, thereby permitting the coating of these photoconductors in large amounts on suitable supporting substrates.

DETAILED DESCRIPTION OF THE INVENTION

The electrophotographic, photoconductive materials of the present invention generally comprise a suitable substrate or supporting layer coated with a photoconductive layer containing the photoconductor material described above.

As a supporting layer, there may be used any suitable backing material. For example, metallic plates composed of aluminum, zinc, copper, tin, iron, lead, etc., may be used. Also, glass plates or other ceramic materials may be utilized. Paper is also a suitable support material. Also, sheets produced from films of synthetic polymeric materials, such as polystyrene, polyethylene, cellulose esters, etc., may be used. Although not necessary for the practice of the present invention, it is sometimes desirable to coat the highly resistive support layers with a conducting material to render the support conductive. For example, the paper and polymeric films employed as the substrates may be coated with a transparent layer of silver, gold or stannous oxide to render them conductive.

The photoconductors of the present invention are coated onto the substrate material according to any of the well known, conventional processes. Generally, the photoconductors are dissolved or dispersed in a suitable organic solvent and uniformly spread on a surface of the support by centrifuging, spraying, brushing or coating. The layer formed is then dried to produce a uniform photoconductive layer on the support surface. Suitable organic solvents are benzene, acetone, methylene chloride, ethylene glycol monomethyl ether, dichloroethane, dioxane, dimethyl-formamide, or mixtures thereof.

Generally, it is desired to incorporate the photoconductive materials in a polymeric matrix on the support layer. This may be accomplished by including in the solution of photoconductor material in the above-described organic solvents a quantity of polymeric material which, upon coating and drying, would yield a layer wherein the photoconductor material is uniformly distributed throughout the polymeric matrix.

As polymeric materials, there may be employed many of the natural and synthetic resins. Suitable natural resins include balsam resins, colophony, shellac, gum arabic, and Manila gum. Micro-crystalline waxes, as well as modified natural substances, such as cellulose diacetate, cellulose triacetate, cellulose acetate butyrate, ethyl cellulose, ethyl cellulose stearates, etc., may also be employed. Synthetic polymers, such as vinyl polymers, for example, polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl acetals, polyvinyl ethers, etc., are also suitable. Other synthetic resinous materials include polyacrylic and polymethacrylic acid esters, polystyrene, polyisobutylene, chlorinated rubber, polyesters, such as phthalate resin, alkyd resin, maleic resinate, maleic resin/colophony, mixed esters of higher alcohols, phenol-formaldehyde resins, aldehyde resins, ketone resins, polyamides, polyurethanes, polyolefins, such as polyethylene, polypropylenes, etc., and silicon resins.

In addition, the photoconductors of the invention may be utilized as sensitizing dyes in conjunction with other photoconductive resins, such as poly-4-vinyldibenzofuran, poly-alpha-methyl styrene, polydimethylamino styrene, polystyrene, poly-1-vinylnaphthalene, polyvinyl carbazole, etc.

Where the photoconductors of the present invention are employed in association with resins, the proportion of

resin to photoconductor may vary over a wide range. Generally, the ratio of photoconductor to resinous material in the final coated electrophotographic product may vary from about 0.2 to about 1.0. The resinous material and the photoconductor may be mixed in any suitable fashion prior to dissolution in the organic solvent or may be added separately to the organic solvent prior to coating on the support material. Optionally, the photoconductor may be first coated on the support material and a layer of the resinous material coated thereover to provide a protective layer.

It is to be understood further that any of the conventional additives, such as pigments, gloss enhancers and stabilizers may be added to the photoconductive layer. One of the advantageous features of the invention, however, is that the photoconductors of the invention are highly colored and possess high photoconductive sensitivities. Accordingly, it is unnecessary to add to these materials the sensitizers, activators and pigments normally required with prior art photoconductors. As a result, the inherent instability of the conventionally employed dyes and sensitizers is avoided.

The photoconductors of the present invention have been found to have a sensitivity comparative to that of selenium, a conventionally employed inorganic photoconductor. Although the sensitivities of these photoconductors are sufficiently high to enable their use in electrophotographic materials alone, the sensitivities may even further increase by the addition thereto of certain activators or electron acceptors. It is to be understood, however, that these activators are not to be confused with the sensitizing dyes normally required in conjunction with the prior art photoconductors. These sensitizing dyes are normally highly unstable, thereby deleteriously affecting the overall composition, even though the sensitivity of the photoconductors is increased. The activators which may be employed in conjunction with the photoconductors of the invention do not contribute to the instability of the system, and are relatively simple compounds in comparison with the prior art sensitizing dyes. Suitable activators include those disclosed in U.S. Pat. No. 3,232,755. Specific activators include 2,2',4,4',6,6'-hexanitrodiphenyl amine; 3,5-dinitrobenzoic acid; tetrabromophthalic anhydride; 2,6-diphenol-p-benzoquinone; 2,4,7-trinitro-9-fluorenone; 4,4',6,6'-tetranitrodiphenic acid; 3,5-dinitrobenzoic acid. These activators may be mixed with the photoconductor and the polymeric matrix material, where used, prior to coating on the support material.

The amount of activator employed is not overly critical and is limited by the dark conductivity. That is, high concentrations of some activators increase the dark conductivity to an extent that the photoconductive element is not useful in electrophotography. Normally, amounts of up to about 20% are sufficient.

The thickness of the electrophotographic, photoconductive layer is not critical. Good results are obtained where the thickness of the layer varies from about 2 to about 20 μ . It will be apparent to those skilled in the art that those layers which are too thin possess insufficient insulating power whereas too thick layers require overlong exposure times.

The reproduction process of the present invention employing the above-described electrophotographic, photoconductive materials may take a variety of forms. According to a first method, a conductive support material coated with the electrophotographic materials of the present invention may be electrostatically charged by friction with a smooth material, corona discharge, contact charge, etc. The electrophotographic layer is subsequently imagewise exposed to electromagnetic radiation of a suitable wave length such that the exposed portions of the layer are discharged and an electrophotographic latent image obtained. This latent image may then be developed according to a variety of methods. According to one method, an electroscopic developing powder is con-

EXAMPLE 22

A formulation of a 5% benzene solution of poly-4-vinyldibenzofuran, with 10% by weight of trinitrofluorenone and 2% by weight of the compound that is used in Example 12 was coated on an aluminum slide using a 5 mil wet gap. The exposure was 0.5 second at 30 inches using a 40 watt bulb. The copy had no background and good image density.

EXAMPLE 23

A formulation of a 5% benzene solution of polyvinyl-naphthylene containing 14% 2,4,7-trinitro-9-fluorenone and 2% of the compound of Example 1 was coated on an aluminum slide using a 3 mil wet gap. The exposure conditions were 0.1 second at 30 inches with a 40 watt bulb. The copy produced had good image density with no background.

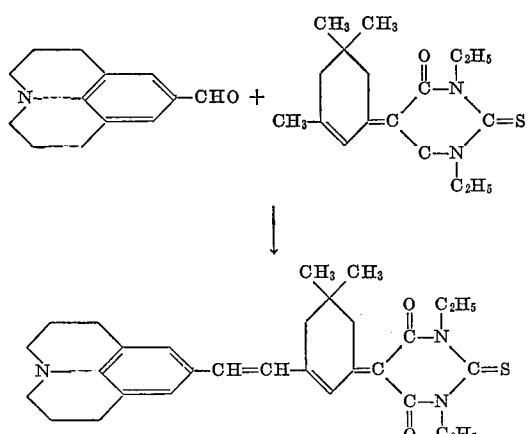
EXAMPLE 24

A formulation of 3 grams of a 7% poly-N-vinylcarbazole solution in dichloroethane, 0.2 gram of the compound used in formulation of Example 1, 2 ml. of dichloroethylene, and .01 gram of hexanitrodiphenylamine was coated on an aluminum slide using a 7 mil wet gap. The exposure conditions were .05 second at 30 inches with a 15 watt bulb. The copy had good density and low background.

The following examples will illustrate methods for the preparation of the photoconductive materials of the present invention.

EXAMPLE 25

1,3 - diethyl - 5[5 - (2,3,6,7 - tetrahydro - (1H,5H)-benzo - (i,j) - quinolizin - 9 - yl) - 1,3 - neopentylene - 2,4-pentadienylidene]-2-thiobarbituric acid was prepared according to the following equation:

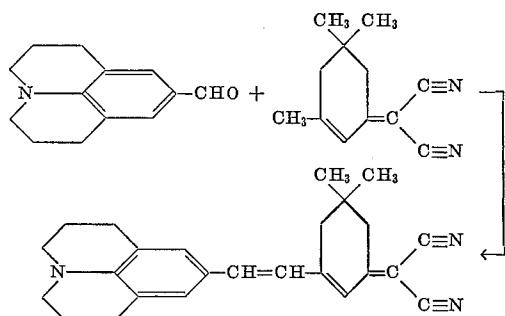


A mixture of 9-formyljulolidine (12 grams; 0.05 mole) and 1,3 - diethyl - 5,3,5,5 - trimethyl - 2,cyclohexane - 1 - ylidene-2-thiobarbituric acid (9.6 grams; 0.03 mole) in ethanol (75 ml.) containing piperidine (6 ml.) was refluxed for 20 minutes, after which methanol (200 ml.) and acetic acid (12 ml.) were added. The reaction mixture was chilled overnight. A black-green solid (5 grams) was filtered off and recrystallized from methylcyclohexane to give dark green crystals having a gold reflex, M.P. 225°. The yield was 33%. An additional 40% yield was obtained from the original solution which was allowed to stand for 72 hours.

1,3 - diethyl - 5 - (3,5,5 - trimethyl - 2 - cyclohexanol-1-ylidene)-2-thiobarbituric acid may be prepared by reacting isophorone and 1,3-diethyl-2-thiobarbituric acid. 9-formyljulolidine may be prepared according to the method described in the Journal of Organic Chemistry, vol. 21, page 1470 (1956).

EXAMPLE 26

[5 - (2,3,6,7 - tetrahydro - 1H,5H - benzo - [i,j]-quinolizin - 9 - yl) - 1,3 - neopentylene - 2,4 - pentadienylidene]-malononitrile may be prepared according to the following equation:

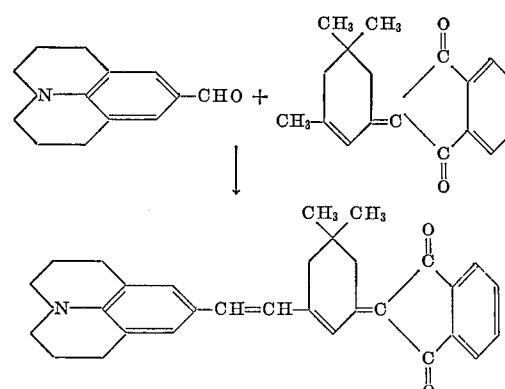


1.86 grams of 3,5,5-trimethyl-2-cyclohexane-1-ylidene-malononitrile and 4 grams of 9-formyljulolidine in ethanol (25 ml.) and piperidine (2 ml.) were refluxed for 20 minutes. 70 ml. of methanol and 4 ml. of acetic acid were then added and the entire mixture placed in a refrigerator. The reaction product was filtered off as a solid and recrystallized from methylcyclohexane. The recrystallized product had a melting point of 223-226° that was obtained in a yield of 35%.

The product was analyzed with the following results. Theoretical: C, 81.74%; H, 6.81%; N, 11.45%. Found: C, 81.73%; H, 6.82% and N, 11.22%. The 3,5,5-dimethyl-2 - cyclohexane - 1 - ylidine - malononitrile may be prepared by reacting isophorone with malononitrile in accordance with the method described in U.S. Pat. No. 2,882,158.

EXAMPLE 27

2 - [5(2,3,6,7 - tetrahydro - 1H,5H - benzo - [i,j]-quinolizin - 9 - yl) - 1,3 - neopentylene - 2,4 - pentadienylidene]-1,3-indanodione was prepared according to the following equation:



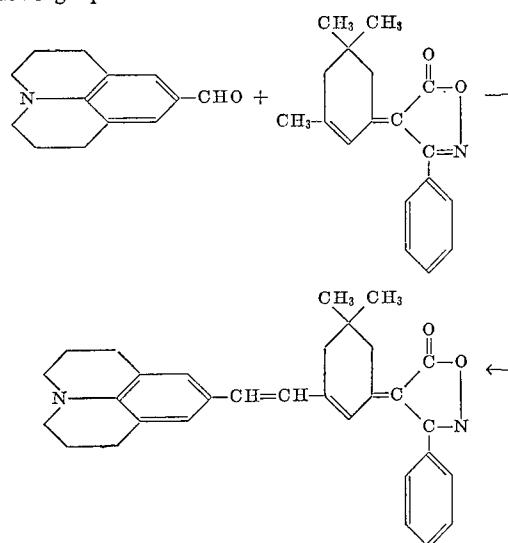
1 gram of 3,5,5-trimethyl-2-cyclohexane-1-ylidene-1,3-indanodione and 1.8 grams 9-formyljulolidine were refluxed in ethanol (25 ml.) with piperidine (1 ml.) for 15 minutes. The mixture was cooled and 2 ml. of acetic acid and 50 ml. of methanol were added. The reaction mixture was placed in a refrigerator whereupon a precipitate formed. The precipitate was filtered and dried and recrystallized from methylcyclohexane. A yield of 18% product was obtained having a melting point of 197-200°.

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The 2,3,5,5 - trimethyl - 2 - cyclohexane,1-ylidene-1,3-indanedione may be prepared by reacting isophorone with indanedione.

EXAMPLE 28

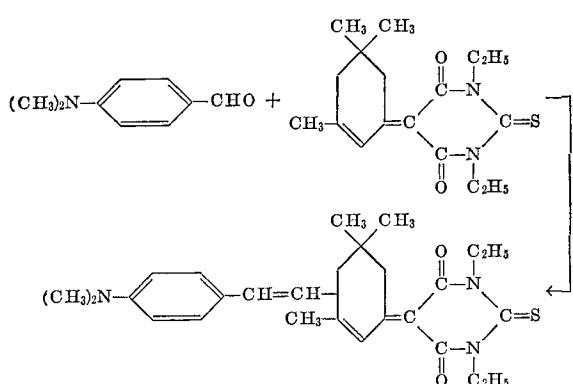
4-[5-(2,3,6,7 - tetrahydro - 1H,5H - benzo-[i,j]-quoliniz - 9 - yl) - 1,3 - neopentylene-2,4-pentadienylidene-3-phenyl-2-isooxazolin-5-one was prepared according to the following equation:



2.81 grams of 3-phenyl-4,3,5,5-trimethyl-2-cyclohexenylidene isooxazolin-5-one and 4 grams of 9-formyljulolidine were refluxed in ethanol (25 ml.) containing piperidine (2 ml.) for fifteen minutes. Acetic acid (4 ml.) was added to the cooled reaction mixture with stirring. The solution was then placed in a refrigerator for several hours until a precipitate formed. The precipitate was filtered and dried and recrystallized from methylcyclohexane. A 29% yield was obtained.

EXAMPLE 29

1,3-diethyl - 5 - paradimethylaminophenyl-1,3-neo-pentylene - 2,4 - pentadienylidene-2-thiobarbituric acid was prepared according to the following equation:

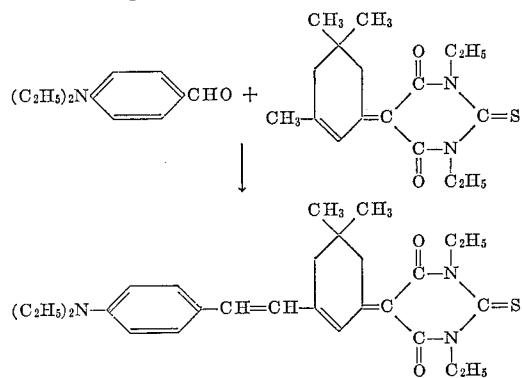


3.2 grams of 1,3-diethyl-5,3,5,5-trimethyl-2-cyclohexen-1-ylidene-2-thiobarbituric acid and 2.8 grams of para-dimethylaminobenzaldehyde were mixed in 25 ml. of absolute ethanol. 2 ml. of piperidine was added and the mixture refluxed with stirring for approximately fifteen minutes. The mixture was poured into a beaker and 100 ml. of methanol was added. The reaction mixture was transferred to a 250 ml. Erlenmeyer flask. To the reaction mixture was added 4 ml. of acetic acid. The mixture was placed in a refrigerator whereupon a precipitate formed. The precipitate was filtered off and dried and recrystallized from methylcyclohexane. Two grams of product was obtained having a melting point of 203-205 degrees.

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EXAMPLE 30

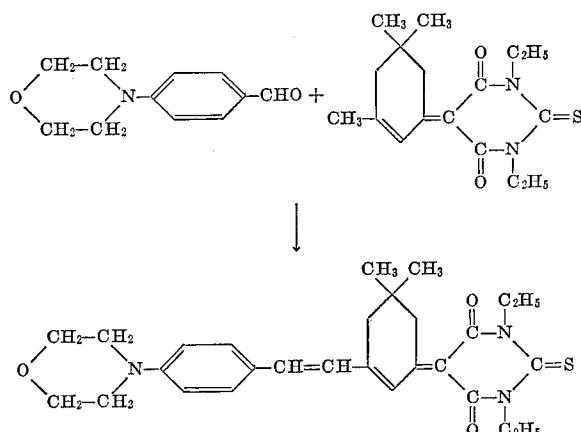
1,3 - diethyl - 5 - para diethylaminophenyl-1,3-neopen-tylene-2,4-pentadienylidene-2-thiobarbituric acid was prepared according to the following equation:



3.2 grams of 1,3-diethyl-5,3,5,5-trimethyl-2-cyclohexen-1-ylidene-2-thiobarbituric acid and 3.54 grams of para-diethylaminobenzaldehyde was mixed in 25 ml. of absolute ethyl alcohol containing 2 ml. of piperidine. The mixture was refluxed with stirring for approximately fifteen minutes and transferred to a 250 ml. Erlenmeyer flask. 100 ml. of methanol and 4 ml. of glacial acetic acid were added and the mixture placed in a refrigerator whereupon a precipitate formed. The precipitate was filtered and dried and recrystallized from methylcyclohexane yielding 1 gram of product having a melting point of 85-87 degrees.

EXAMPLE 31

1,3 - diethyl - 5 - paramorpholinophenyl-1,3-neopen-tylene-2,4-pentadienylidene-2-thiobarbituric acid was prepared according to the following equation:



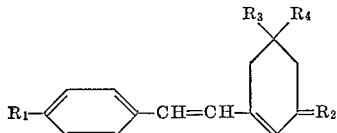
1.91 grams of morpholinobenzaldehyde and 1.6 grams of 1,3 - diethyl-5,3,5,5-trimethyl-2-cyclohexen-1-ylidene-2-thiobarbituric acid was mixed with stirring in 25 ml. of ethyl alcohol. 2 ml. of piperidine was added and the mixture refluxed with stirring for twenty minutes. 100 ml. of ethyl alcohol and 4 ml. of glacial acetic acid were added and the mixture placed in a refrigerator whereupon a precipitate formed. The precipitate was filtered off, washed with methanol, dried and recrystallized from methylcyclohexane. The product was obtained in a yield of 40 percent and had a melting point of 153-154 degrees.

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

What is claimed is:

1. An electrophotographic photoconductive composi-

tion containing a photoconductor having the structural formula:



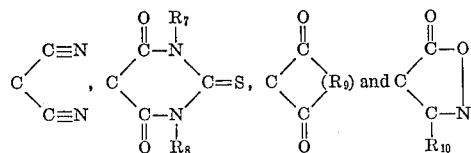
wherein:

R₁ is selected from the group consisting of



morpholino, thiomorpholino, piperidino and julolidylinyl;

R₂ is selected from the group consisting of:



R₃, R₄, R₅, R₆, R₇ and R₈ may be the same or different and are lower alkyl groups;

R₉ is the residue of a one, two or three fused ring aryl group such that the ring is a five membered ring; and R₁₀ is selected from the group consisting of aryl and substituted aryl groups.

2. The composition of claim 1 wherein said photoconductor is the sole photoconductive substance.

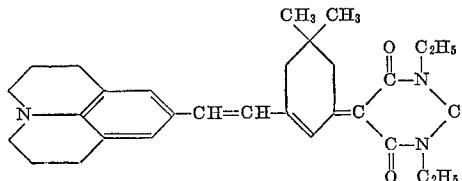
3. The composition of claim 1 wherein said photoconductor is employed as a sensitizer for an organic photoconductive substance.

4. An article comprising a support layer and a photoconductive insulating layer containing the photoconductor of claim 1.

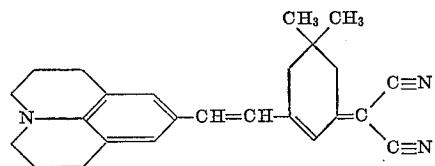
5. The composition of claim 1 wherein said photoconductor is suspended in a polymeric matrix.

6. The composition of claim 1 additionally containing an activator, said activator being an electronic acceptor for the photoconductor of claim 1.

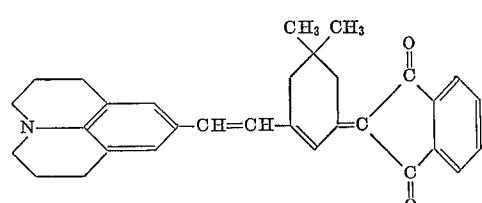
7. The electrophotographic composition of claim 1 wherein said photoconductor has the formula



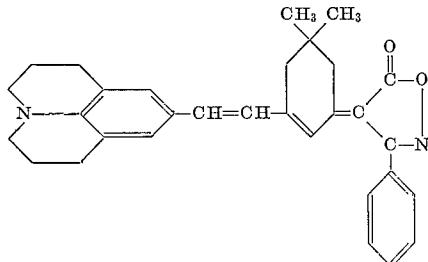
8. The electrophotographic composition of claim 1 wherein said photoconductor has the formula



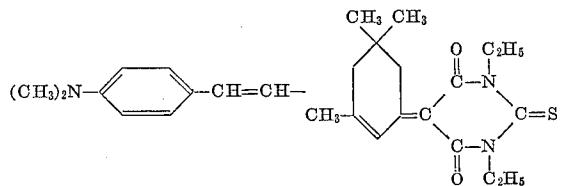
9. The electrophotographic composition of claim 1 wherein said photoconductor has the formula



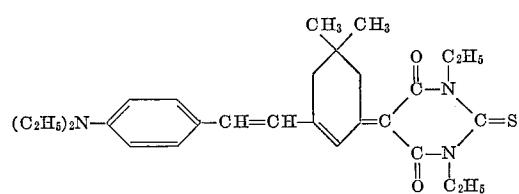
10. The electrophotographic composition of claim 1 wherein said photoconductor has the formula



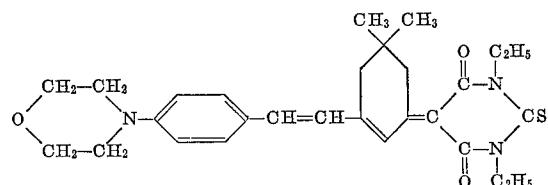
11. The electrophotographic composition of claim 1 wherein said photoconductor has the formula



12. The electrophotographic composition of claim 1 wherein said photoconductor has the formula



13. The electrophotographic composition of claim 1 wherein said photoconductor has the formula



14. An electrophotographic reproduction process comprising forming an electrostatic charge pattern on the photoconductive composition of claim 1 and developing said charge pattern.

15. The process of claim 14 wherein said charge pattern is formed by exposing said photoconductive composition to light and subsequently electrically charging said photoconductive composition.

16. The process of claim 14 wherein said charge pattern is formed by electrically charging said photoconductive composition and subsequently exposing said charged composition to light.

17. The process of claim 15 including the steps of fixing said developed image.

18. An electrophotographic photoconductive composition as defined in claim 1 wherein R₃, R₄, R₅, R₆, R₇ and R₈ are methyl.

References Cited

UNITED STATES PATENTS

3,232,755 2/1966 Hoegl et al. 96-1

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252—501; 260—243, 247, 251, 260, 269, 293