

[54] **NOVEL XEROGRAPHIC PLATE
CONTAINING PHOTOINJECTING
POLYNUCLEAR QUINONE PIGMENTS**

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abandoned.

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96/1.6

[51] Int. Cl. **G03g 5/06**

[58] Field of Search **96/1.5, 1 R, 1 PC, 1.5 C;**
252/501

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Primary Examiner—Norman G. Torchin

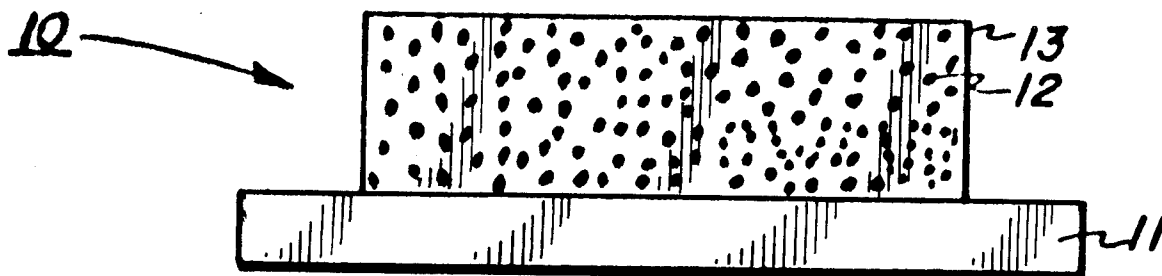
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[57] **ABSTRACT**

An electrophotographic plate having a photoreceptor comprising a photoinjecting pigment selected from the class of polynuclear quinone pigments and an active transport material which is substantially transparent in the wavelength region of xerographic use and capable of supporting charge carrier injection from the pigment. The photoinjecting polynuclear quinone pigments have the property of being efficient both in photogeneration of charge carriers and subsequent injection of the charge carriers into hole and electron active transport materials. The photoinjecting pigment and active transport material system may be used in a binder or layer type photoreceptor. The structure may be imaged in the conventional xerographic mode which usually includes charging, exposure to light, and development.

22 Claims, 3 Drawing Figures



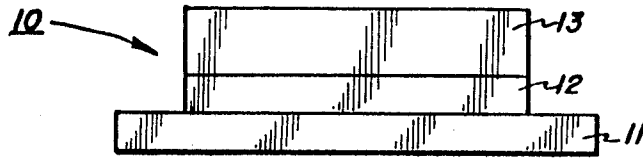


FIG. 1

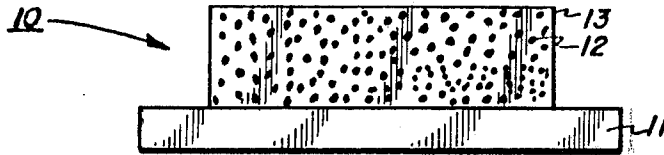


FIG. 2

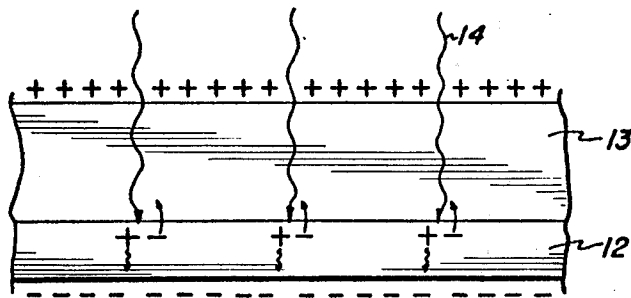


FIG. 3

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NOVEL XEROGRAPHIC PLATE CONTAINING PHOTOINJECTING POLYNUCLEAR QUINONE PIGMENTS

This application is a continuation of application Ser. No. 94,066, filed Dec. 1, 1970, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates in general to xerography and more specifically to a novel photosensitive device and method of use.

In the art of xerography, a xerographic plate containing a photoconductive insulating layer is imaged by first uniformly electrostatically charging its surface. The plate is then exposed to a pattern of activating electromagnetic radiation such as light, 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 to form a visible image by depositing finely divided electroscopic marking particles on the surface of the photoconductive insulating layer.

A photoconductive layer for use in xerography may be a homogeneous layer of a single material such as vitreous selenium or it may be a composite layer containing a photoconductor and another material. One type of composite photoconductive layer used in xerography is illustrated by U.S. Pat. No. 3,121,006 to Middleton and Reynolds which describes a number of binder layers comprising finely-divided particles of a photoconductive inorganic compound dispersed in an electrically insulating organic resin binder. In its present commercial form, the binder layer contains particles of zinc oxide uniformly dispersed in a resin binder and is coated on a paper backing.

In the particular examples of binder systems described in Middleton et al., the binder comprises a material which is incapable of transporting injected charge carriers generated by the photoconductor particles for any significant distance. As a result, with the particular materials disclosed in the Middleton et al. patent, the photoconductor particles must be in substantially continuous particle-to-particle contact throughout the layer in order to permit the charge dissipation required for cyclic operation. With the uniform dispersion of photoconductor particles described in Middleton et al., therefore, a relatively high volume concentration of photoconductor, up to about 50 percent or more by volume, is usually necessary in order to obtain sufficient photoconductor particle-to-particle contact for rapid discharge. It has been found, however, that high photoconductor loadings in the binder layers of the resin type result in the physical continuity of the resin being destroyed, thereby significantly reducing the mechanical properties of the binder layer. Layers with high photoconductor loadings are often characterized by a brittle binder layer having little or no flexibility. On the other hand, when the photoconductor concentration is reduced appreciably below about 50 percent by volume, the discharge rate is reduced, making high speed cyclic or repeated imaging difficult or impossible.

U.S. Pat. No. 3,121,007 to Middleton et al. teaches another type of photoconductor which includes a two phase photoconductive binder layer comprising photoconductive insulating particles dispersed in a homo-

neous photoconductive insulating matrix. The photoconductor is in the form of a particulate photoconductive inorganic crystalline pigment broadly disclosed as being present in an amount from about 5 to 80 percent by weight. Photodischarge is said to be caused by the combination of charge carriers generated in the photoconductive insulating matrix material and charge carriers injected from the photoconductive crystalline pigment into the photoconductive insulating matrix.

U.S. Pat. No. 3,037,861 to Hoegl et al. teaches that polyvinyl carbazole exhibits some long-wave U. V. sensitivity and suggests that its spectral sensitivity be extended into the visible spectrum by the addition of dye sensitizers. Hoegl et al. further suggests that other additives such as zinc oxide or titanium dioxide may also be used in conjunction with polyvinyl carbazole. In Hoegl et al., it is clear that the polyvinyl carbazole is intended to be used as a photoconductor, with or without additive materials which extend its spectral sensitivity.

In addition, certain specialized layer structures particularly designed for reflex imaging having been proposed. For example, U.S. Pat. No. 3,165,405 to Hoesterey utilizes a two layered zinc oxide binder structure for reflex imaging. The Hoesterey patent utilizes two separate contiguous photoconductive layers having different spectral sensitivities in order to carry out a particular reflex imaging sequence. The Hoesterey device utilizes the properties of multiple photoconductive layers in order to obtain the combined advantages of the separate photoresponse of the respective photoconductive layers.

It can be seen from a review of the conventional composite photoconductive layers cited above, that upon exposure to light, photoconductivity in the layer structure is accomplished by charge transport through the bulk of the photoconductive layer, as in the case of vitreous selenium (and other homogeneous layer modifications). In devices employing photoconductive binder structures, which include inactive electrically insulating resins such as those described in the Middleton et al., 3,121,006 patent, conductivity or charge transport is accomplished through high loadings of the photoconductive pigment allowing particle-to-particle contact of the photoconductive particles. In the case of photoconductive particles dispersed in a photoconductive matrix, such as illustrated by the Middleton et al., 3,121,007 patent, photoconductivity occurs through the generation of charge carriers in both the photoconductive matrix and the photoconductor pigment particles.

Although the above patents rely upon distinct mechanisms of discharge throughout the photoconductive layer, they generally suffer from common deficiencies in that the photoconductive surface during operation is exposed to the surrounding environment, and particularly in the case of cycling xerography, susceptible to abrasion, chemical attack, heat, and multiple exposures to light during cycling. These effects are characterized by a gradual deterioration in the electrical characteristics of the photoconductive layer resulting in the printing out of surface defects and scratches, localized areas of persistent conductivity which fail to retain an electrostatic charge, and high dark discharge.

In addition to the problems noted above, these photoconductive layers require that the photoconductor comprise either a hundred percent of the layer, as in the case of the vitreous selenium layer, or that they

preferably contain a high proportion of photoconductive material in the binder configuration. The requirements of a photoconductive layer containing all or a major proportion of a photoconductive material further restricts the physical characteristics of the final plate, drum or belt in that the physical characteristics such as flexibility and adhesion of the photoconductor to a supporting substrate are primarily dictated by the physical properties of the photoconductor, and not by the resin or matrix material which is preferably present in a minor amount.

Another form of composite photosensitive layer which has also been considered by the prior art includes a layer of photoconductive material which is covered with a relatively thick plastic layer and coated on a supporting substrate.

U.S. Pat. No. 3,041,166 to Bardeen describes such a configuration in which a transparent plastic material overlays a layer of vitreous selenium which is contained on a supporting substrate. The plastic material is described as one having a long range for charge carriers of the desired polarity. In operation, the free surface of the transparent plastic is electrostatically charged to a given polarity. The device is then exposed to activating radiation which generates a holeelectron pair in the photoconductive layer. The electron moves through the plastic layer and neutralizes a positive charge on the free surface of the plastic layer thereby creating an electrostatic image. Bardeen, however, does not teach any specific plastic materials which will function in this manner, and confines his examples to structures which use a photoconductor material for the top layer.

French Pat. No. 1,577,855 to Herrick et al. describes a special purpose composite photosensitive device adapted for reflex exposure by polarized light. One embodiment which employs a layer of dichroic organic photoconductive particles arrayed in oriented fashion on a supporting substrate and a layer of polyvinyl carbazole formed over the oriented layer of dichroic material. When charged and exposed to light polarized perpendicularly to the orientation of the dichroic layer, the oriented dichroic layer and polyvinyl carbazole layer are both substantially transparent to the initial exposure light. When the polarized light hits the white background of the document being copied the light is depolarized, reflected back through the device and absorbed by the dichroic photoconductive material. In another embodiment, the dichroic photoconductor is dispersed in oriented fashion throughout the layer of polyvinyl carbazole.

In view of the state of the art, it can readily be seen that there is a need for a general purpose photoreceptor exhibiting acceptable photoconductive characteristics and which additionally provides the capability of exhibiting outstanding physical strength and flexibility to be reused under rapid cyclic conditions without the progressive deterioration of the xerographic properties due to wear, chemical attack, and light fatigue.

OBJECTS OF THE INVENTION

It is an object of this invention to provide a novel electrophotographic plate having a photoreceptor member containing photoconductors which overcomes the above noted disadvantages.

Another object of the present invention is to provide a novel electrophotographic imaging device having

photosensitive pigments which are capable of highly efficient charge generation and injection.

Another object of this invention is to provide photoinjecting pigments which are useful with either electron or hole active transport materials.

It is still another object of this invention to provide an operably efficient photoreceptor portion of an electrophotographic member having relatively small amounts of photosensitive material.

It is yet another object to provide a novel imaging system.

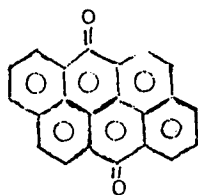
SUMMARY OF THE INVENTION

The foregoing objects and others are accomplished in accordance with this invention by providing an electrophotographic plate having a photoreceptor member, comprising active transport material, which is capable of supporting photogenerated charge injection and transport, and a photoinjecting pigment which has a high efficiency of photogeneration of charge carriers and effective charge injection capability into said transport material. The photoinjecting pigments of the instant invention have maximum photoresponse in the wavelength region in which most active transport materials are substantially transparent. In addition, these photoinjecting pigments are capable of injecting either photo-excited electrons or holes into the appropriate active transport materials with extraordinarily high efficiency under conditions of a practical applied field. The active transport material to be used in conjunction with the photoinjecting pigments of the instant invention may be any material capable of supporting either hole or electron injection, provided it is substantially non-absorbing in the particular wavelength region of xerographic use which will coincide with the region in which the photoconductor is photosensitive.

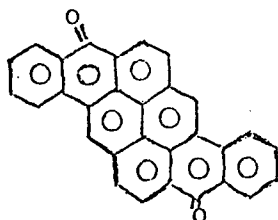
It should be understood that the active transport material does not function as a photoconductor in the wavelength region of use. As stated above, hole-electron pairs are photogenerated in the photosensitive pigment and the electrons are then injected across a field modulated barrier into the active transport material and electron transport occurs through said active transport material.

In accordance with the present invention it has been found that a xerographic or electrophotographic sensitive member can be prepared utilizing a photoinjecting pigment selected from the class of polynuclear quinone pigments in conjunction with electrostatically active transport materials of either an electron or hole transport type. The term, polynuclear quinone, applies to a series of compounds having a structure which appears to be the condensation of a quinone residue with an aromatic residue.

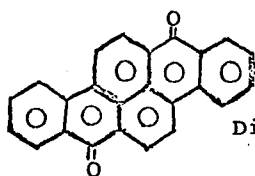
It has now been found that polynuclear quinones, which are well known as pigments, have both efficient photogeneration and injection characteristics with active transport materials. The most useful polynuclear quinones in such systems have been found to be anthraquinone derivatives, flavanthrones, and polynuclear quinones having more than three condensed aromatic rings. These classes of polynuclear quinone pigments are preferred because of their commercial availability and high photosensitivity. From these classes of polynuclear quinone pigments, the following compounds have produced optimum results:



Anthranthrone

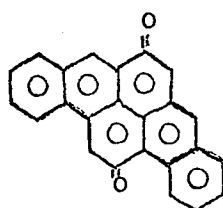
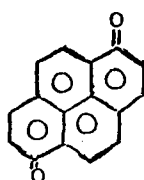


Pyranthrone

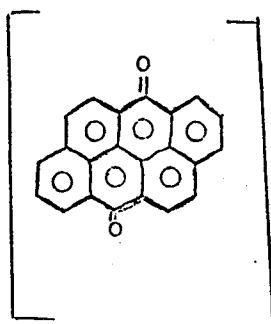


Dibenzpyrenequinones

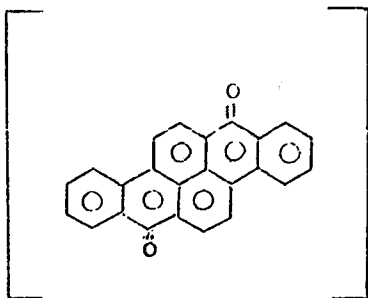
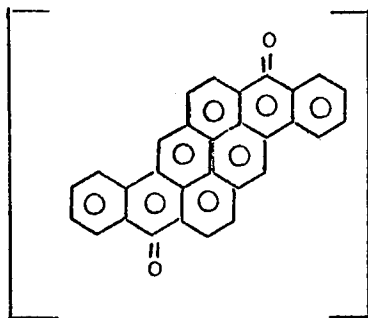
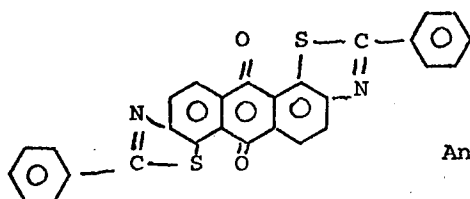
Pyrenequinone



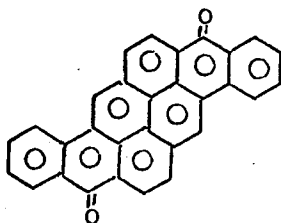
3,4,9,10-dibenzpyrenequinone

Brominated
Anthanthrone Br_2

7

 Br_2 Brominated
DibenzpyrenequinoneBrominated
Pyranthrone Br_2 

Anthraquinone Thiazoles



Flavanthrone

While the aforementioned polynuclear quinones are preferred, any other polynuclear quinone, or mixtures thereof, may be used where suitable. Typical polynuclear quinones include benzanthrone acridenes; acridone carbazoles, dinaphthaloylacridones, and mixtures thereof.

The polynuclear quinone pigments of the instant invention are to be distinguished from other photosensitive materials of the prior art in that they are efficient in photogeneration and injection, and, in addition, have

excellent compatibility with most hole and electron active transport materials, thereby enabling the use of a relatively low applied field in the corresponding xerographic photoreceptor member to effect suitable injection and gain. The polynuclear quinone pigments of the present invention also have optimum photosensitivity in the wavelength region of from about 4000 to 6000 Angs. Units which is the area of xerographic use over which an appropriate active transport material must have a degree of transparency. By contrast, many photoconductors of the prior art, while being photosensi-

tive in this wavelength region, have not been found to be sufficiently compatible with useful electronically active transport materials and are thereby inefficient with respect to injection of photogenerated charges into the surrounding or adjacent active transport material. Therefore the use of said photoconductive materials in combination with active transport materials requires an impractical applied field in excess of 5×10^5 volts/cm. Because of their unique properties the photoinjecting pigments of the instant invention can be used with transport materials in relatively small quantities in either a layered or binder structure xerographic photoreceptor.

A typical application of the instant invention consists of a supporting substrate such as an electrical conductor containing a photoconductor layer overcoated with an active transport material. For example, the photoconductor layer may comprise pyanthrone, a polynuclear quinone, overcoated with a relatively thick layer of electron acceptor material such as 2,4,7-trinitro-9-fluorenone (TNF), which is substantially transparent in the wavelength region of from about 4000 to 6000 Angs. Units and capable of supporting electron injection and transport. The distinctive nature of the pigment as well as its compatibility with the active transport material enables the use of a relatively thin layer of the polynuclear quinone without any loss of efficiency.

DESCRIPTION OF THE DRAWINGS

Further objects of the invention, together with additional features contributing thereto will be apparent from the following description of one embodiment of the invention when read in conjunction with the accompanying drawings wherein:

FIG. 1 is a schematic sectional view of another embodiment of another xerographic member contemplated by the instant invention.

FIG. 2 is a schematic sectional view of another embodiment of another xerographic member contemplated by the instant invention.

FIG. 3 illustrates a discharge mechanism of injection by the photoconductive pigments of the instant invention.

DETAILED DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates one embodiment in the improved xerographic plate 10 according to this invention. Reference character 11 designates a substrate or mechanical support. The substrate may comprise a metal which is brass, aluminum, gold, platinum, steel or the like. It may be of any convenient thickness, rigid or flexible, in the form of a sheet, web, cylinder, or the like, and may be coated with a thin blocking layer. It may also comprise such other materials as paper, metallized paper, plastic sheets covered with a thin coating of aluminum or copper oxide, or glass coated with a thin layer of chromium or tin oxide. It is usually preferred that the support member be somewhat electrically conductive or have a somewhat conductive surface and that it be strong enough to permit a certain amount of handling. In certain instances, however, support 11 need not be conductive or may even be dispensed with entirely.

Reference character 12 designates a photoconductive single or unitary layer which includes the photoinjecting polynuclear quinone pigments of the instant invention. In particular the single layer comprises a poly-

nuclear quinone pigment selected from the group of anthraquinone derivatives, flavantrones, and polynuclear quinones having more than three condensed aromatic rings. The photoinjecting polynuclear quinones of the aforementioned group have the property of being efficient photogenerators and injectors of charge carriers into either hole transport or electron transport active transport materials.

Photoconductive single layer 12 of FIG. 1 may be of any suitable thickness used for carrying out its function in the xerographic insulating member. Thicknesses for this purpose range from 0.05 to 20 microns. Thicknesses about 20 microns tend to produce undesirable positive residual buildup in the pigment layer during the cycling and excessive dark decay, while thicknesses below 0.05 microns become inefficient in absorbing impinging radiation. A range of from about 0.2 to 5 microns is preferred since these thicknesses would insure maximum functionality of the photoconductor with a minimum amount of said pigment substance and avoid the above mentioned problems with regard to thicknesses.

While reference character 12 of FIG. 1 designates a photoconductive single layer of photoinjecting pigment it is within the purview of the instant invention that said layer may comprise photoinjecting pigment dispersed in a matrix material. The matrix material may be any suitable organic substance used for such purposes including inert matrix or binder materials or one of the presently used active transport materials. The concentration of the photoconductor material will vary according to which type of binder material is used and will range in value from about 5 to 99 volume percent of the total photoconductive layer. If an electronically inert binder material is used in combination with the photoinjecting pigments of volume ratio of at least 25 percent photoconductor to the electronically inert binder material is necessary to effect particle-to-particle contact or proximity thereby rendering layer 12 photoconductive throughout. The remarks with regard to thickness of the photoconductive single layer of FIG. 1 are applicable here; namely, a range of from about 0.05 to 20 microns, with a range of 0.2 to 5 microns being preferred, due to the variations of pigment concentration in the binder layer.

Because the photoreceptors of the instant invention will be exposed to a wavelength region corresponding to the range of photoresponse of the pigment this will be the particular wavelength region to which the active transport material must be substantially transparent. As heretofore mentioned the photoinjecting polynuclear quinone pigments described in the present invention have optimum photoresponse in the wavelength region of from about 4000 to 6000 Angs. Units, the area of xerographic use of the present pigment-transport photoreceptor. Therefore exposure to a light source having this wavelength region of emission enables the pigment to function at its maximum efficiency in absorbing all impinging radiation and creating charge carriers.

Reference character 13 designates the active transport layer which overlies the photoinjecting pigment single layer 12. As pointed out above, the active transport material can be either an electron or hole transport due to the distinctive nature and effectiveness of the photoinjecting polynuclear quinones of the instant invention. Consistent with what has been said previ-

ously, the active transport material to be used with the polynuclear quinone pigments of the present invention must be substantially transparent in the wavelength region of photoresponse of the pigment which region is the particular area of xerographic use. The polynuclear quinone pigments of the present invention are photore-
sponsive in the wavelength region of from about 4000 to 6000 Angstrom. The active transport materials de-
scribed, are particularly useful with polynuclear quino-
nes of the instant invention. These include hole
transport materials such as carbazole, N-ethyl carba-
zole, N-isopropyl carbazole, N-phenyl-carbazole, tetra-
raphenylpyrene, 1-methylpyrene, perylene, chrysene,
anthracene, tetrathene, 2-phenyl naphthalene, azapy-
rene, fluorene, fluorenone, 1-ethylpyrene, acetyl py-
rene, 2,3-benzochrysene, 3,4-benzopyrene, 1,4-
bromopyrene, and phenyl-indole, polyvinyl carbazole,
polyvinyl pyrene, polyvinyl tetracene, polyvinyl pery-
lene, and polyvinyl tetrathene. Suitable electron trans-
port materials include 2,4,7-trinitro-9-fluorenone
(TNF), 2,4,5,7-tetranitrofluorenone, dinitroanthra-
cene, dinitroacridene, tetracyanopyrene, and dinitroanthraquinone.

It will be obvious to those skilled in the art that the use of any polymer which contains the appropriate aromatic or heterocyclic moiety charge carrier transport such as carbazole, tetrathene, pyrene, 2,4,7-trinitro-9-fluorenone, etc., will function as an active transport material. It is not the intent of the invention to restrict the type of polymer which can be employed as the transport material. Polyesters, polysiloxanes, polyamides, polyurethanes, and epoxies, as well as block, random or graft copolymers (containing the aromatic moiety) are exemplary of the various types of polymers which could be employed. In addition, electronically inactive polymers in which the active moiety is dispersed at high concentration can be employed.

Thi thickness of the active transport layer is not critical to the function of the xerographic member. However, the thickness of said active transport layer would be dictated by practical needs in terms of the amounts of electrostatic charge necessary to induce an applied suitable to effect electron injection and transport. Active transport layer thicknesses of from about 5 to 100 microns would be suitable, but thicknesses outside this range may be used. The ratio of the thickness of the active transport layer to the photoconductor layer should be maintained from about 2:1 to 200:1.

The substantial or significant transparency of the active transport material within the context of the instant invention, as exemplified by FIG. 1, means that a sufficient amount of radiation from a source must pass through the active transport layer 13, in order that the photoconductive layer 12, can function in its capacity as a photogenerator and injector of charge carriers. More specifically, significant transparency is present in the wavelength region of from about 4000 to 6000 Angstrom Units impinges the pigment layer so as to cause discharge of a charged pigment-active transport photoreceptor.

It is not the intent of this invention to strictly restrict the choice of active transport materials to those which are transparent in the entire visible region. For example, when the layered structure of FIG. 1 is used with a transparent substrate, imagewise exposure may be accomplished through the substrate without the light passing through the layer of active transport material.

In this case the active material need not be non-absorbing in the wavelength region of use. This particular application takes advantage of the injection properties of the present photoinjecting pigments and falls within the purview of the instant invention. Other applications where complete transparency is not required for the active material include the selective recording of narrowband radiation such as that emitted from lasers, spectral pattern recognition, color coded form duplication, and possible color xerography.

While the active transport layer 13 of FIG. 1 may consist exclusively of charge transport material, for purposes of the present invention, the layer may also comprise the charge transport material dispersed at a sufficient concentration in a suitable inert binder material to effect particle-to-particle contact or to effect sufficient proximity thereby permitting effective charge transport from the photoinjecting pigments of the instant invention through the layer. Generally there must be a volume ratio of at least 25 percent active transport material to electronically inert binder material to obtain the desired particle-to-particle contact or proximity. Typical resin binder materials for the practice of the invention are polystyrene; silicone resins such as DC-801, DC-804, and DC-996 all manufactured by the Dow Corning Corporation, Lexan, a polycarbonate, and SR-82 manufactured by the General Electric Company; acrylic and methacrylic ester polymers such as Acryloid A10 and Acryloid B72, polymerized ester derivatives of acrylic and alpha-acrylic acids both supplied by Rohm and Haas Company, and Lucite 44, Lucite 45 and Lucite 46 polymerized butyl methacrylates supplies by the E. I. du Pont de Nemours & Company; chlorinated rubber such as Parlon supplied by the Hercules Powder Company; vinyl polymers and copolymers such as polyvinyl chloride, polyvinyl acetate, etc. including Vinylite VYHH and VMCH manufactured by the Bakelite Corporation; cellulose esters and ethers such as ethyl cellulose, nitrocellulose, etc.; alkyd resins such as Glyptal 2469 manufactured by the General Electric Company; etc. In addition, mixture of such resins with each other or with plasticizers so as to improve adhesion, flexibility, blocking, etc. of the coatings may be used. Thus, Rezyl 869 (a linseed oil-glycerol alkyd manufactured by American Cyanamid Company) may be added to chlorinated rubber to improve its adhesion and flexibility. Similarly, Vinylites VYHH and VMCH (polyvinyl chloride-acetate copolymers manufactured by the Bakelite Company) may be blended together. Plasticizers include phthalates, phosphates, adipates, etc. such as tricresyl phosphate, dioctyl phthalate, etc. as is well known to those skilled in the plastics art.

Another embodiment of the instant invention is illustrated in FIG. 2. Here the photoreceptor layer 10 consists of photoinjecting pigment particles 12 contained in an active transport matrix binder 13. In general, to attain the best combination of physical and electrical properties, the upper limit for the photoconductive pigment or particles must be about 5 percent by volume of the active transport binder layer. A lower limit for the photoconductive particles of about 0.1 percent by volume of the binder layer is required to insure that the light absorption coefficient is sufficient to give appreciable carrier generation.

The thickness of the binder layer is not particularly critical. Layer thicknesses from about 2 to 100 microns have been found satisfactory, with a preferred thick-

ness of about 5 to 50 yielding particularly good results.

The size of the photosensitive particles is not particularly critical in the binder structure, but particles in a size range of about 0.01 to 1.0 microns yield particularly satisfactory results.

While the layered configuration as described in FIG. 1 differs structurally from the binder photoreceptor of FIG. 2, the functional relationship of the photosensitive material to the active transport material is the same in that there is photogeneration in the photosensitive particles and subsequent injection into the surrounding active transport material. Therefore any description of the layered configuration of FIG. 1, given above, relating to the nature of the materials and the interactions with each other are applicable here with the exception that, because of the proximity of the photosensitive particles, to the surface of the photoreceptor the binder plate is preferably charged in the same polarity as the photogenerated charges which can be transported by the active transport material. Therefore if electron transport material is being used as a binder then the plate is preferably charged negatively while positive charging is preferred in the case of hole transport material. In addition, the condition of substantial transparency of the active transport material is necessary here to insure maximum functionality of the binder structure.

Another variation of the structures of FIGS. 1 and 2 consists of the use of a blocking layer at the substrate-photoreceptor interface. Such a blocking layer serves first to reduce potential leakage in the absence of activating radiation, which leakage is known in the art as "dark decay." In addition, the blocking layer aids in sustaining an electric field across the photoreceptor after the charging step. Any suitable blocking material may be used in thicknesses of from about 0.1 to 1 micron. Typical materials include nylon, epoxy, aluminum oxide and insulating resins of various types including polystyrene, butadiene polymers and copolymers, acrylic and methacrylic polymers, vinyl resins, alkyd resins, and cellulose base resin.

Reference character 13 in FIGS. 1 and 2 designate the active charge transport material which acts as either an overlayer or a binder for the photoinjecting pigment material 12. As heretofore mentioned, the charge transport material is capable of supporting charge injection from the pigment particles, or layer, and transporting said photogenerated charges under the influence of an applied field. In order to function in the manner outlined above, the active transport material should be substantially transparent, or non-absorbing, to the particular wavelength region of pigment photosensitivity. With regard to the polynuclear quinones of the present invention the charge transport material should be substantially non-absorbing in the visible part of the electromagnetic spectrum which ranges from about 4000 to 6000 Angstrom Units because the xerographically useful polynuclear quinone pigments have maximum photoresponse to wavelengths in this region.

The active transport material which is employed in conjunction with the photoconductive pigments in the instant invention is a material which is an insulator to the extent that an electrostatic charge placed on the charge transport material is not conducted in the absence of illumination at a rate to prevent the formation and retention of an electrostatic latent image thereon.

In general, this means that the specific resistivity of the active transport material should be at least 10^{10} ohms-cm. and preferably will be several orders higher. For optimum results, however, it is preferred that the specific resistivity of the active matrix material be such that overall resistivity of the photoreceptor, in the absence of activating illumination or charge injection from the photoconductive pigments, be about 10^{12} ohms-cm.

In summary, it is clear that the photoinsulating portion of the xerographic members of the instant invention represented in FIGS. 1 and 2 is divided into two functional components:

1. A photoinjecting pigment which photogenerates charge carriers upon excitation by radiation within a particular wavelength region and injects said photogenerated charge carriers into the adjacent active transport material, and;

2. A substantially transparent active transport material which allows transmission of radiation to the photoinjecting pigment, accepts the subsequently photogenerated charge carriers from the photosensitive material, and actively transports these charge carriers to an oppositely charged surface or substrate to effect neutralization.

This is more graphically illustrated by a simplified mechanism in FIG. 3 where an electron-transport layered structure has been positively charged by means of corona charging. The activating radiation represented by the arrows 14 then passes through the transparent active transport layer and impinges the pigment layer thereby creating a hole-electron pair. The electron and hole are then separated by the force of the applied field and the electron injected across the interface into the active transport layer. There the photogenerated electron is transported by force of the electrostatic attraction through the active transport system to the surface where it neutralizes the positive charge previously deposited by means of corona charging. Since only photogenerated electrons can move in the presently illustrated electron acceptor active transport layer, large changes in surface potential can result only when the electric field in the layered structure is such as to move the photogenerated electrons from the photoconductor layer to the charged surface. It is necessary therefore that in a layered configuration illustrated by FIG. 1 that an electron transport material photoreceptor by charged positively and a hole-transport material photoreceptor be charged negatively. As pointed out above the opposite is true when the system is a binder layer as illustrated in FIG. 2.

DESCRIPTION OF PREFERRED EMBODIMENTS

For purposes of affording those skilled in the art and a better understanding of the invention, the following illustrative examples are given:

EXAMPLE I

A plate or layered structure similar to that illustrated in FIG. 1 is prepared as follows:

1. A nylon coated aluminum substrate is maintained at room temperature while a 0.8 micron thick layer of dibenzoquinone is vacuum evaporated thereon.

2. A 17 percent polymer stock solution is prepared by dissolving the appropriate amount of polyvinyl carbazole (Luvican M170 grade poly-N-vinyl carbazole (PVK) from the BASF Chemical Company) in a solu-

tion of 180 grams of toluene and 20 grams of cyclohexanone.

3. A 7 micron PVK layer is then formed by applying the stock solution of PVK to the dibenzopyrenequinone pigment layer using a Gardner Laboratories Bird 5 Applicator. Finally the resulting photoreceptor is air dried at 110°C for from 2 to 24 hours.

EXAMPLE II

A series of 7 additional plates are made by the 10 method of Example I using the following photoinjecting pigments as the photoconductive layer: (a) anthanthrone, (b) pyranthrone, (c) pyrenequinone, (d) 3,4,9,10-dibenzpyrenequinone, (e) brominated anthrone, (f) brominated dibenzpyrenequinone, (g) brominated pyranthrone, (h) flavanthrone, and (i) Algol Yellow, an anthraquinone thiazole, manufactured by 15 the General Aniline and Film Company of New York.

The plates made in Examples I and II were tested 20 electrically by the following technique: The samples are charged by negative corona charging to a potential of about 500 volts. The samples are then exposed to a monochromatic discharge light corresponding to a wavelength area in which each pigment has photore- 25 sponse. Since the photoinjecting pigments of the instant invention have maximum photoresponse, $\lambda_{\max}$, in the visible region of the electromagnetic spectrum from about 4000 to 6000 Angs. Units the photoreceptors are exposed to a tungsten lamp filtered by an interference filter with a 100 Angs. Unit band width, having 30 its peak transmittance at about 4500 Angs. Units. Additional measurements are taken with other filters having transmission peaks spaced about evenly through the entire region of from 4000 to 6000 Angs. The initial 35 voltage and resulting discharge, measured as $(dV/dt)_{T=0}$ in each individual photodischarge experi-

ment in monitored by a DC-type loop probe which is connected to a Keithley 610B electrometer to measure the voltages as a function of time resulting in a plot of photoresponse vs. field. From these experiments the maximum gain (G) and the threshold field E_T , that is, 5 that field which gives rise to the lowest detectable discharge, are obtained. In addition, from the initial discharge rate the gain (G) may be calculated.

The experimental methodology and the means of calculation are outlined by P. Regensburger in "Optical Sensitization of Charge Carrier Transport in PVK," Photochemistry and Photobiology, 8, p. 429-40 (November, 1968). Briefly, the gain is determined by plotting the initial xerographic gain (G) as a function of the 15 applied field. The xerographic gain was calculated from the initial discharge rate

$$G = (dV/dt)_{t=0} / (eId/\epsilon)$$

where I is the incident photon flux, d the thickness of 20 the layer, ϵ the electric permittivity, and e , the electronic charge. A xerographic gain of unity would be observed if one charge carrier per incident photon were excited and moved across the layer.

As can be seen from the results outlined in Table I 25 the plates exhibit good xerographic maximum gains of up to 70 percent. Also all the pigments require a relatively low threshold field going as low as 1 volt/micron which indicates that the photoinjecting pigments of the instant invention are capable of functioning under oper- 30 ating conditions of most xerographic machines. In addition, the high discharge rates confirm what has been previously stated concerning the efficient photogenerated charge injection properties of the polynuclear quinone pigments. The dissipation of the negatively charged PVK surface graphically illustrates the 35 efficiency of hole injection into the active layer.

TABLE I

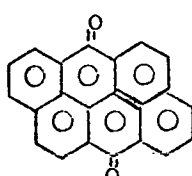
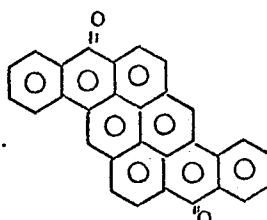
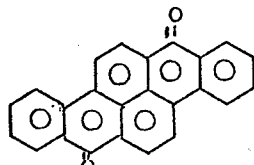
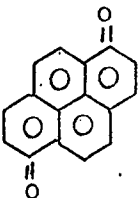
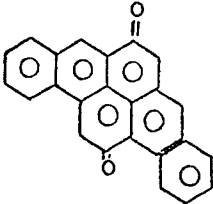
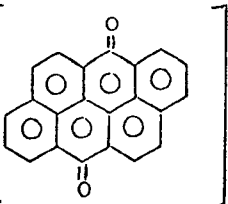
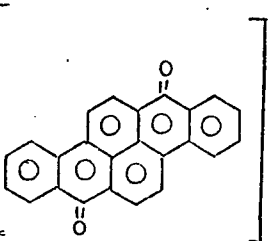
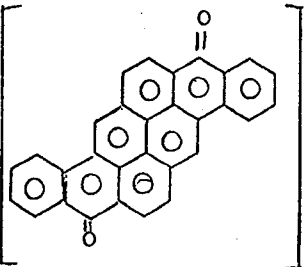
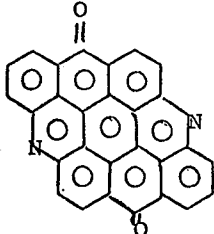
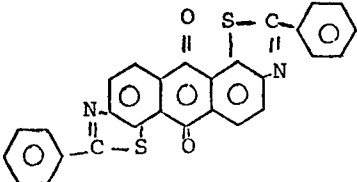
TABLE 1		$\lambda_{\max}$	$G_{\max}$	E_T (V/u)	$(dv/dt)_{t=0}$ neg.
Anthanthrone		395	0.37	2.5	1145
Pyranthrone		454	0.25	1.7	3107
Dibenzpyrene-quinone		408	0.35	2.4	4390

Table I—Continued

		λ_{max}	G_{max}	E_T (V/u)	$(dV/dt)_{t=0}$ neg.
Pyrenequinone		408	0.20	29.0	606
3,4,9,10-dibenz- pyrenequinone		(O) ₂ 454	0.10	5.5	967
Brominated anthanthrone		(Br) ₂ 522	0.08	2.5	852
Bromiated dibenzpyrene- quinone		(Br) ₂ 408	0.70	1.6	6340
Brominated pyranthrone		(Br) _x 454	0.35	5.0	2507
Flavanthrone		408	0.34	2.5	1500
Algol Yellow		400	0.10	1	1740

As heretofore mentioned, the photoinjecting pigments of the present invention can be used with electron transport active transport materials. In carrying out experiments with an electron transport photoreceptor having the instant photoinjecting pigments the surface is positively charged and measurements conducted in the same manner outlined in Examples I and II. It is found that the electron transport photoreceptors have similar xerographic properties as the hole transport materials demonstrated in Table I; that is, there are acceptable xerographic gains and relatively low threshold fields.

The present invention has been described with reference to certain specific embodiments which have been presented in illustration of the invention. It is to be understood however that numerous variations of the invention may be made and that it is intended to encompass such variation within the scope and spirit of the invention as described by the following claims.

What is claimed is:

1. an electrophotographic plate having a photoreceptor binder layer consisting essentially of photoconductive particles dispersed in an active transport binder in an unoriented fashion in an amount of from about 0.1 to 5 percent by volume of said binder, said binder and particles being compatible so as to support efficient photogenerated charge injection from said photoconductive particles, said photoconductive particles comprising a pigment selected from anthanthrone, dibenzpyrenequinone, brominated dibenzpyrenequinone, brominated pyranthrone, and flavanthrone, and said active transport binder consisting essentially of a material selected from the group consisting of electron transport and hole transport materials, said binder material being capable of supporting the injection and transport of photogenerated charges from said photoconductive particles through said binder material and being substantially transparent in the wavelength region of from about 4000 to 6000 Angstrom Units, and wherein said active transport binder has a thickness of from about 5 to 100 microns.

2. The electrophotographic plate of claim 1 in which the active transport material is selected from the group of hole transport materials consisting of carbazole, N-ethylcarbazole, N-isopropyl carbazole, N-phenylcarbazole, tetraphenylpyrene, 1-methylpyrene, perylene, chrysene, fluorene, fluorenone, anthracene, tetracene, tetraphene, 2-phenylanthracene, azapyrene, 1-ethylpyrene, acetyl pyrene, 2,3-benzochrysene, 2,4-benzopyrene, 1,4-bromopyrene and phenyl indole, polyvinyl carbazole, polyvinyl pyrene, polyvinyl tetracene, polyvinyl perylene, and polyvinyl tetraphene.

3. The electrophotographic plate of claim 1 in which the active transport material is selected from the group of electron transport substances consisting of 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitrofluorenone, dinitroanthracene, dinitroacridene, tetracyanopyrene, dinitroanthraquinone, and polymeric materials thereof.

4. The electrophotographic plate of claim 1 in which the pigment is anthanthrone.

5. The electrophotographic plate of claim 1 in which the pigment is dibenzpyrenequinone.

6. The electrophotographic plate of claim 1 in which the pigment is brominated dibenzpyrenequinone.

7. The electrophotographic plate of claim 1 in which the pigment is brominated pyranthrone.

8. The electrophotographic plate of claim 1 in which the pigment is flavanthrone.

9. An electrophotographic plate having at least two adjacent layers said layers consist essentially of an unoriented photoconductive layer overlaying a substrate member with a layer of an active transport material overlaying said photoconductive layer, both of said layers being compatible so as to support efficient photogenerated charge injection from said photoconductive layer, said photoconductive layer comprising a photoinjecting pigment selected from anthanthrone, dibenzpyrenequinone, brominated dibenzpyrenequinone, brominated pyranthrone and flavanthrone, and said active transport material consisting essentially of a material selected from the group consisting of electron transport and hole transport materials, said material being capable of supporting the injection and transport of photogenerated charges from said photoconductive material through said material and being substantially transparent in the wavelength region of from about 4000 to 6000 Angs. Units, and wherein said active transport layer has a thickness of from about 5 to 100 microns, said photoconductor layer has a thickness of from 0.05 to 20 microns, and the ratio of the thickness of the active transport layer to the photoconductor layer is from about 2:1 to 200:1.

10. The electrophotographic plate of claim 9 in which the active transport material is selected from the group of hole transport materials consisting of carbazole, N-ethylcarbazole, N-isopropyl carbazole, N-phenylcarbazole, tetraphenylpyrene, 1-methylpyrene, perylene, chrysene, fluorene, fluorenone, anthracene, tetracene, tetraphene, 2-phenylanthracene, azapyrene, 1-ethylpyrene, acetyl pyrene, 2,3-benzochrysene, 2,4-benzopyrene, 1,4-bromopyrene and phenyl indole, polyvinyl carbazole, polyvinyl pyrene, polyvinyl tetracene, polyvinyl perylene, and polyvinyl tetraphene.

11. The electrophotographic plate of claim 9 in which the active transport material is selected from the group of electron-transport substances consisting of 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitrofluorenone, dinitroanthracene, dinitroacridene, tetracyanopyrene, dinitroanthraquinone, and polymeric materials thereof.

12. The electrophotographic plate of claim 9 in which the pigment is anthanthrone.

13. The electrophotographic plate of claim 9 in which the pigment is dibenzpyrenequinone.

14. The electrophotographic plate of claim 9 in which the pigment is brominated dibenzpyrenequinone.

15. The electrophotographic plate of claim 9 in which the pigment is brominated pyranthrone.

16. The electrophotographic plate of claim 9 in which the pigment is flavanthrone.

17. A method of imaging which comprises:

a. providing an electrophotographic plate having a photoreceptor binder layer consisting essentially of photoconductive particles dispersed in an active transport binder in an unoriented fashion in an amount from about 0.1 to 5 percent by volume of said binder, said binder and particles being compatible so as to support efficient photogenerated charge injection from said photoconductive particles, said photoconductive particles comprising a pigment selected from anthanthrone, dibenzpyrenequinone, brominated dibenzpyrenequinone, brominated pyranthrone, and flavanthrone.

none, brominated pyranthrone, and flavanthrone, and said active transport binder material consisting essentially of a material which is capable of supporting the injection and transport of photogenerated charges from said photoconductive particles through said binder material which is substantially transparent in the wavelength region of from about 4200 to 6500 Angs., and wherein said active transport binder has a thickness of from about 5 to 100 microns.

b. uniformly charging said plate, and

c. exposing said plate to a source of radiation in the wavelength region of from about 4200 to 6500 Angs. whereby injection and transport of photogenerated charges from said photoconductive particles occurs through said active transport binder to form an electrostatic image on the surface of said plate.

18. The method of claim 17 which further includes developing said latent image to make it visible.

19. The method of claim 17 in which the substrate is substantially transparent and exposure is carried out through said substrate.

20. A method of imaging which comprises:

a. providing an electrophotographic plate having at least two adjacent layers, said layers consisting essentially of an unoriented photoconductive layer overlaying a substrate member with a layer of an active transport material overlaying said photoconductive layer, both of said layers being compatible so as to support efficient photogenerated charge

injection from said photoconductive layer, said photoconductive layer comprising a photoinjecting pigment selected from anthanthrone, dibenzpyrenequinone, brominated dibenzpyrenequinone, brominated pyranthrone, and flavanthrone, and said active transport layer consisting essentially of a material which is capable of supporting the injection and transport of photogenerated charges from said photoconductive layer through said transport layer which is substantially transparent in the wavelength region of from about 4200 to 6,500 Angs., and wherein said active transport layer has a thickness of from about 5 to 100 microns, said photoconductor layer has a thickness of from 0.05 to 20 microns and the ratio of the thickness of the active transport layer to the photoconductor layer is from about 2:1 to 200:1.

b. uniformly charging said plate, and

c. exposing said plate to a source of radiation in the wavelength region of from about 4200 to 6500 Angs. whereby injection and transport of photogenerated charges from said photoconductive layer occurs through said active transport layer to form an electrostatic image on the surface of said plate.

21. The method of claim 20 which further includes developing said latent image to make it visible.

22. The method of claim 20 in which the substrate is substantially transparent and exposure is carried out through said substrate.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,877,935

Dated April 15, 1975

Inventor(s) Paul J. Regensburger and James J. Jakubowski

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

- Column 2, line 34 "laayer" should be --layer--.
- Column 3, line 26 "holeelectron" should be --hole-electron--;
line 36 "adaapted" should be --adapted--.
- Column 4, line 6 "it" should be --It--;
line 27 "photo-exicted" should be --photo-excited--.
- Column 11, line 8 "Angstrom" should be --Angstroms--;
line 38 "Thi" should be --The--;
line 42-43 "applied suitable" should be --applied field suitable--.
- Column 14, line 19 "Aa" should be --A--;
line 48 "by" should be --be--;
line 68 "Chemcial" should be --Chemical--.
- Column 16, line 1 "in" should be --is--;
line 17 $G = (dv/dt)_{t=0} / (eId/\epsilon)$ should be
-- $G = \frac{(dv/dt)_{t=0}}{(eId/\epsilon)}$ --
- Column 19, line 21 "an" should be --An--.
- Column 20, line 9 "saaaid" should be --said--;
line 32 "fluroenone" should be --fluorenone--.
- Column 22, line 13 "hhas" should be --has--.

Signed and Sealed this

seventh Day of October 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks