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3,667,944

## QUINACRIDONE PIGMENTS IN ELECTRO- PHOTOGRAPHIC RECORDING

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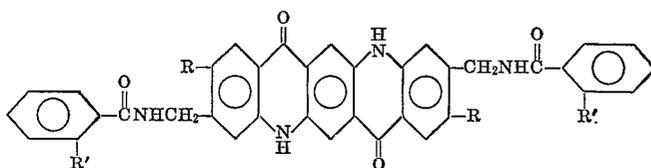
Int. Cl. G03g 5/06

U.S. Cl. 96—1 PC

6 Claims

### ABSTRACT OF THE DISCLOSURE

An electrophotographic plate including a photoconductive layer comprising a novel quinacridone pigment in a binder material, said quinacridone pigment having the formula:



wherein R=CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub> or a halogen and wherein R'=COOH, COOCa/2, SO<sub>3</sub>H, or SO<sub>3</sub>Ca/2 is disclosed. Methods of preparing said plate and of using said plate in electrophotographic processes are also disclosed.

### BACKGROUND OF THE INVENTION

This invention relates, in general, to electrophotography and, more specifically, to a binder plate usable in electrophotography.

It is known that images may be formed and developed on the surface of certain photoconductive insulating materials by electrostatic means. The basic electrophotographic process, as taught by Carlson in U.S. Pat. 2,297,691, involves uniformly charging a photoconductive insulating layer and then exposing said layer to a light-and-shadow images which dissipates the charge on the portions of the layer which are exposed to light. The electrostatic latent image formed on the layer corresponds to the configuration of the light-and-shadow image. Alternatively, a latent electrostatic image may be formed on the plate by charging said plate in image configuration. This image is rendered visible by depositing on the imaged layer a finely divided developing material comprising a colorant called a toner and a toner carrier. The powdered developing material will normally be attracted to those portions of the layer which retain a charge, thereby forming a powder image corresponding to the latent electrostatic image. Where the base sheet is relatively inexpensive, such as paper, the powder image may be fixed directly to the plate as by heat or solvent fusing. Alternatively, the powder image may be transferred to a sheet of receiving material, such as paper, and fixed thereon. The above general process is also described in U.S. Pats. 2,357,809; 2,891,011; and 3,079,342.

The photoconductive insulating layer to be effective must be capable of holding an electrostatic charge in the dark and dissipating the charge to a conductive substrate when exposed to light. That various photoconductive insulating materials may be used in making electrophotographic plates is known. Suitable photoconductive insulating materials such as anthracene, sulfur, selenium or mixtures thereof have been disclosed by Carlson in U.S. Pat. 2,297,691. These materials generally have sensitivity in the blue or near ultraviolet range, and all but selenium have a further limitation of being only slightly light-sensitive. For this reason, selenium has been the most commercially accepted material for use in electro-

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photographic plates. Vitreous selenium, however, while desirable in most aspects, suffers from serious limitations in that its spectral response is somewhat limited to the ultra-violet, blue and green regions of the spectrum and the preparation of vitreous selenium plates requires costly and complex procedures, such as vacuum evaporation. Also, vitreous selenium layers are only metastable in that they are readily recrystallized into inoperative crystalline forms at temperatures only slightly in excess of those prevailing in conventional electrophotographic copying machines. Further, selenium plates require the use of a separate conductive substrate layer, preferably with an additional barrier layer deposited thereon before deposition of the selenium photoconductor. Because of these economic and commercial considerations, there have been

many recent efforts toward developing photoconductive insulating materials other than selenium for use in electrophotographic plates.

It has been proposed that various two-component materials be used in photoconductive insulating layers used in electrophotographic plates. These consist of a photoconductive insulating material in particulate form dispersed in an insulating binder. Where the particles consist of a photoconductive material comprising inorganic crystalline compounds containing a metallic ion, satisfactory photographic speed and spectral response for use in xerographic plates are obtained. However, these plates even when dy-sensitized generally have sensitivities much lower than selenium. These plates are generally considered to be non-reusable since it is necessary to use such high percentages of photoconductive pigment in order to attain adequate sensitivity that it is difficult to obtain smooth surfaces which lend themselves to efficient toner transfer and subsequent cleaning prior to reuse. An additional drawback in the use of inorganic pigment-binder type plates is that they can be charged only by negative and not by positive corona discharge. This property makes them commercially undesirable since negative corona discharge generates much more ozone than positive corona discharge and is generally more difficult to control.

It has been further demonstrated that organic photoconductive dyes and a wide variety of polycyclic compounds may be used together with suitable resin materials to form photoconductive insulating layers useful in binder-type plates. These plates generally lack sensitivity levels necessary for use in conventional electrophotographic copying devices. In addition, these plates lack abrasion resistance and stability of operation, particularly at elevated temperatures.

In another type plate, inherently photoconductive polymers are used frequently in combination with sensitizing dyes or Lewis acids, to form photoconductive insulating layers. These polymeric organic photoconductor plates generally have the inherent disadvantages of high cost of manufacture, brittleness, and poor adhesion to supporting substrates. A number of these photoconductive insulating layers have thermal distortion properties which make them undesirable in an automatic electrophotographic apparatus which often includes powerful lamps and thermal fusing devices which tend to heat the electrophotographic plate.

Thus, there is a continuing need for improved photoconductive insulating materials from which stable, sensitive, and reusable electrophotographic plates can be made.

## SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide an electrophotographic plate devoid of the above-noted disadvantages.

Another object of this invention is to provide electrophotographic plates having sensitivities which extend over substantial portions of the visible spectrum.

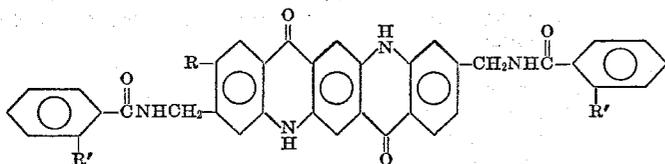
Still another object of this invention is to provide a reusable electrophotographic plate having a high overall sensitivity and high thermal stability when compared to present commercially available reusable plates.

Yet another object of this invention is to provide a photoconductive insulating material suitable for use in electrophotographic plates in both single use and reusable systems.

Yet another object of this invention is to provide a photoconductive insulating layer for an electrophotographic plate which is substantially resistant to abrasion and has a relatively high distortion temperature.

Yet another further object of this invention is to provide an electrophotographic plate having a wide range of useful physical properties.

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing an electrophotographic plate having a novel photoconductive layer comprising a quinacridone pigment in a resin binder, said quinacridone pigment having the following general formula:



where  $R = \text{CH}_3, \text{C}_2\text{H}_5, \text{OCH}_3, \text{OC}_2\text{H}_5$  or a halogen and  $R' = \text{COOH}, \text{COOCa}/2, \text{SO}_3\text{H},$  or  $\text{SO}_3\text{Ca}/2$ . This particular class of quinacridone pigments as well as methods for their preparation are fully described in copending application, Ser. No. 772,596, filed in the U.S. Patent Office Nov. 1, 1968.

The above-described quinacridone-resin photoconductive layer may be deposited on any suitable supporting substrate, or may be cast as a self-supporting film. The plate may be overcoated with any suitable materials, if desired. The quinacridone-resin photoconductive layer may be used in the formation of multi-layer sandwich configurations adjacent a dielectric layer, similar to that shown by Golovin et al., in the publication entitled "A New Electrophotographic Process, Effected by Means of Combined Electric Layers" Doklady, Akad. Nauk SSSR vol. 129, No. 5, pages 1008-1011, November-December 1959. It has been found that the percentage of the particular class of quinacridones described above which are required to produce adequate sensitivity in a plate is very low. Because of this, the mechanical properties of the photoconductive layers are substantially determined by the properties of the binder. A wide variety of resin binders may be used in the present invention, varying from soft thermoplastics to hard cross-linked enamels. Thus, the physical properties of the final photoconductive layer may be varied over wide limits by selection of the appropriate resins to suit specific requirements. In this regard, these photoconductive layers are superior to many heretofore known binder suspensions of inorganic pigments which require a relatively high percentage of inorganic pigment such that the inorganic pigment used essentially controls the physical properties of the final photoconductive layer. Since the percentage of quinacridone pigment needed is relatively low, the photoconductive plate may have a very hard, very smooth surface. This eliminates many of the disadvantages of the prior pigment-binder plates which, because of the high proportions of pigment, had a very rough and abrasive surface.

While any of the novel class of quinacridones having the above-described general formula may be used to prepare the photoconductive layer of the present invention, it is preferred to employ those quinacridones wherein R is selected from the group consisting of  $\text{CH}_3, \text{C}_2\text{H}_5$  and mixtures thereof and wherein  $R' = \text{SO}_3\text{Ca}/2$ , since these materials are highly photosensitive and produce the most desirable images.

Various of the above-described quinacridones may be utilized alone or in combination with other compositions in any suitable mixture, dimer, trimer, oligomer, polymer, copolymer or mixtures thereof.

Any suitable organic binder resin may be used in combination with the novel class of quinacridones to prepare the photoconductive layer of this invention. In order to be useful the resin used in the present invention should be more resistive than about  $10^{10}$ , and preferably more than  $10^{12}$  ohms per centimeter under the conditions of electrophotographic use. Typical resins include: thermoplastics including olefin polymers such as polyethylene and polypropylene; polymers derived from dienes such as polybutadiene, polyisobutylene, and polychloroprene; vinyl and vinylidene polymers such as polystyrene, styrene-acrylonitrile copolymers, acrylonitrile-butadiene-styrene terpolymers, polymethylmethacrylate, polyacrylates, polyacrylics, polyacrylonitrile, polyvinylacetate, polyvinyl alcohol, polyvinylchloride, polyvinylcarbazole, polyvinyl ethers, and polyvinyl ketones; fluorocarbon polymers

such as polytetrafluoroethylene and polyvinylidene fluoride; heterochain thermoplastics such as polyamides, polyesters, polyurethanes, polypeptides, casein, polyglycols, polysulfides, and polycarbonates; and cellulosic polymers such as regenerated cellulose, cellulose acetate and cellulose nitrate. Also, thermosetting resins including phenolic resins; amino resins such as urea-formaldehyde resins and melamine-formaldehyde resins; unsaturated polyester resins; epoxy resins, silicone polymers; alkyd resins and furan resins. Various copolymers and mixtures of the above-mentioned resins may be used where applicable. In addition to the above-noted resins, any other suitable material may be used if desired.

The quinacridone compositions of the present invention may be incorporated into the dissolved or melted binder-resin by any suitable means such as strong shear agitation, preferably with simultaneous grinding. Typical methods include ball milling, roller milling, sand milling, ultrasonic agitation, high speed blending and any combination of these methods. Any suitable ratio of pigment to resin may be used. On a quinacridone-dry resin weight basis, the useful range extends from about 1:1 to about 1:40. Best results are obtained at, and therefore the preferred range is, from about 1:4 to about 1:10. Optimum results are obtained when the ratio is about 1:4. While highest photosensitivity is obtained at pigment-resin ratios of 1:1 to 1:4, at the higher concentrations of pigment dark conductivity increases. The optimum balance between sensitivity and dark decay occurs at a ratio of about 1:4. It should be noted that the proportion of photoconductor used in the preferred range lies substantially below that used in making heretofore known inorganic photoconductive binder plates. In these known plates, satisfactory electrophotographic sensitivity is attained only when the pigment-resin ratio is at least 2:1.

The use in the present invention of lower pigment to resin ratios represents a highly desirable advantage over the prior art since a smaller amount of the relatively expensive pigment component is required. Also, this permits

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very smooth adhesive coatings to be obtained because of the high binder content. The small proportion of added material has little effect on the physical properties of the binder-resin. Thus, resins may be chosen having the desired softening range, smoothness, hardness, toughness, solvent resistance, or solubility and the like with assurance that the pigment will not affect these properties to any considerable extent.

When it is desired to coat the quinacridone-resin film on a substrate, various supporting materials may be used. Suitable materials for this purpose include aluminum, steel, brass, metallized or tin oxide coated glass,

semi-conductive plastics and resins, paper and any other convenient material of bulk conductivity at the time of use  $>10^8$  (ohms-cm.)<sup>-1</sup>, or surface conductivity  $>10^8$  mho/square. The pigment-resin-solvent slurry (or the pigment-resin-melt) may be applied to conductive substrates by any of the well-known painting or coating methods, including spraying, flow-coating, knife coating, electro-coating, Mayer bar drawdown, dip coating, reverse roll coating, etc. Spraying in an electric field may be preferred for smoothest finish and dip coating may be preferred for convenience in the laboratory. The setting, drying, and/or curing steps for these plates are generally similar to those recommended for films of the particular binders as used for other painting applications. For example, quinacridone-epoxy plates may be cured by adding a cross-linking agent and stoving according to approximately about the same schedule as other baking enamels made with the same resins and similar pigments for paint application. A very desirable aspect of quinacridone compositions is that they are stable against chemical decomposition at the temperatures normally used for a wide variety of bake-on enamels, and therefore, may be incorporated in very hard glossy photoconductive coatings, having surfaces similar to automotive or kitchen appliance resin enamels.

The thickness of the quinacridone-binder films may be varied from about 1 to about 100 microns, depending upon the required characteristics. Self-supporting films, for example, cannot be conveniently manufactured in

thickness thinner than about 10 microns, and are easiest to handle and use in the 15 to 75 micron range. Coatings, on the other hand, are preferably formed in the 5 to 30 micron range. For some compositions and purposes, it is desirable to provide a protective overcoating. This overcoating should usually not exceed the thickness of a photoconductive coating and preferably should be no more than  $\frac{1}{4}$  the thickness of said coating. Any suitable overcoating, as for example, nitrocellulose lacquer, may be employed.

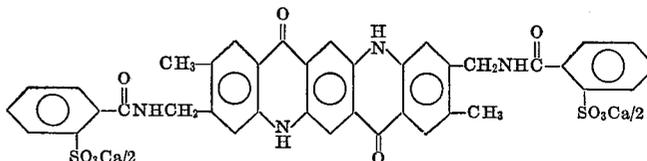
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## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples will further define various preferred embodiments of the present invention. Parts and percentages are by weight unless otherwise specified.

### EXAMPLE I

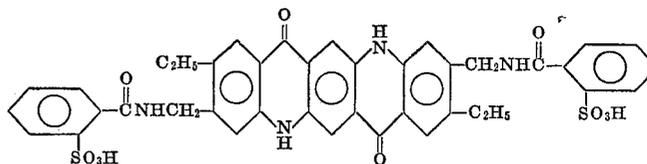
An electrophotographic plate is prepared by initially mixing about 6 parts Pliolite S5B, a styrene-butadiene copolymer resin available from Goodyear Tire and Rubber Company, about 43 parts xylene and about 1 part of a quinacridone pigment having the formula



This mixture is put into a glass jar containing a quantity of  $\frac{1}{8}$  inch steel balls and milled on a Red Devil Quickie Mill (Gardner Laboratories) for about  $\frac{1}{2}$  hour in order to obtain a homogeneous dispersion. After milling, the dispersion is applied to a sheet of 5 mil aluminum foil using a No. 36 wire draw-down rod. The coating, about 20 microns thick, is then forced air dried at about 100° C. for about two hours. The plate is then charged to a positive potential of about 650 volts by means of corona discharge, as described, for example, in U.S. Pat. 2,777,957. The charged plate is then contact exposed for 15 seconds to a film positive by means of a tungsten lamp having a 3400° K. color temperature. The illumination level at the exposure plane is about 57 foot candles. The latent electrostatic image formed on the plate is then developed by cascading pigmented electroscopic marking particles over the plate, by the process described, for example, in U.S. Pat. 2,618,551. The powder image developed on the plate is electrostatically transferred to a receiving sheet and heat fused thereon. The image on the receiving sheet is of very good quality and corresponds to the contact exposed original.

### EXAMPLE II

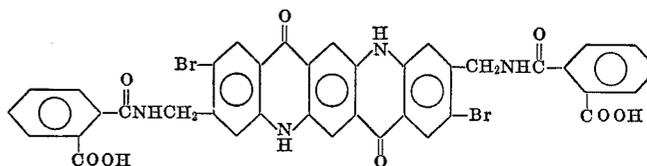
An electrophotographic plate is prepared by initially mixing about 2 parts Silicone SR-82, a methyl-phenyl silicone resin available from General Electric Company, about 40 parts xylene, and about 1 part of a quinacridone pigment having the formula:



This plate is positively charged to an initial potential of about 290 volts, exposed and developed. The image resulting is of satisfactory quality.

### EXAMPLES III-IV

Two electrophotographic plates are prepared by mixing about 1 part Vinylite VYNS, a copolymer of vinyl chloride and vinyl acetate available from Union Carbide Corporation, about 10 parts diethyl ketone and about 1 part of a quinacridone pigment having the formula:

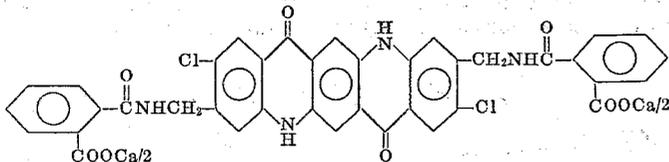


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The plate is coated, cured, charged, exposed and developed as in Example I above, however, in Example III, the plate is positively charged to a potential of 480 volts and, in Example I, the plate is charged to a negative potential of 835 volts. The resulting image is of good quality.

## EXAMPLES V-VI

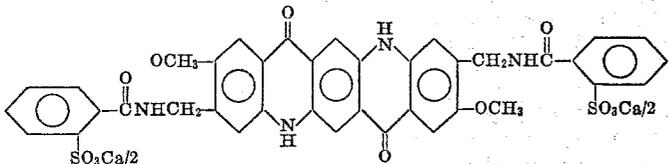
Two electrophotographic plates are prepared by initially mixing about 1 part of Vinylite VYNS, about 10 parts diethyl ketone and about 1 part of a quinacridone pigment having the formula:



The plate is coated, cured, charged, exposed and developed as in Example I above. However, here the plate of Example V is charged to a positive potential of 530 volts and the plate of Example VI is charged to a negative potential of 630 volts. Good images result.

## EXAMPLES VII-VIII

An electrophotographic plate is prepared by initially mixing about 1 part Vinylite VYNS, about 10 parts diethyl ketone, and about 1 part of a quinacridone pigment having the formula:



The plate is coated, cured, charged and developed as in Example I above. However, here the plate of Example VII is charged to a positive potential of 410 volts and the plate of Example VIII is charged to a negative potential of 605 volts. Good images are produced by these plates.

## EXAMPLES IX-X

Two electrophotographic plates are prepared by initially mixing about 100 parts of a 10 percent solution of poly-

vinyl carbazole in benzene, about 5 parts cyclohexanone, and about 1 part of the quinacridone pigment of Example I. These plates are coated, cured, charged, exposed and developed as in Example I above. However, here the plate of Example IX is charged to a positive potential of about 180 volts and the plate of Example X is charged to a negative potential of about 215 volts. Images of good quality are produced.

## EXAMPLES XI-XII

Electrophotographic plates are prepared by initially mixing about 100 parts of a 10 percent polyvinyl carbazole

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solution in benzene, about 5 parts cyclohexanone and about 1 part of the quinacridone pigment of Example II. The plates are coated, cured, charged, exposed and developed as in Example I above. However, here the plate of Example XI is charged to a positive potential of about 150 volts and the plate of Example XII is charged to a negative potential of about 180 volts. Images of good quality result.

Although specific components in proportions have been described in the above examples relating to the use of a novel class of quinacridone pigments in electrophoto-

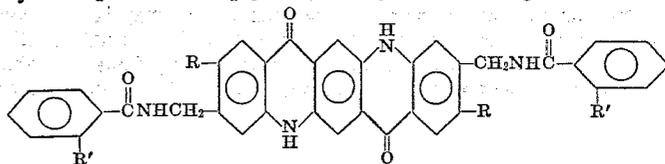
graphic plates, other suitable materials, as listed above, may be used with similar results. In addition, other materials may be added to the quinacridone pigment compositions or to the pigment-resin compositions to synergize, enhance, or otherwise modify their properties. The pigment compositions and/or the pigment-resin compositions of this invention may be dyesensitized, if desired, or may be mixed or otherwise combined with other photoconductors, both organic and inorganic.

Other modifications and ramifications of the present invention will occur to those skilled in the art upon a

reading of the present disclosure. These are intended to be included within the scope of this invention.

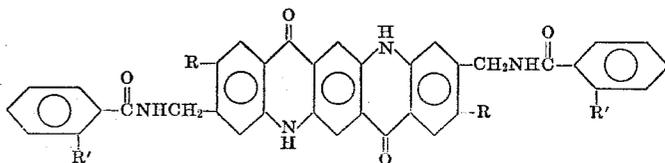
What is claimed is:

1. An electrophotographic imaging process which comprises uniformly charging the surface of an electrophotographic plate comprising a self-supporting layer of an electrophotographic composition comprising a photoconductive quinacridone pigment in a binder material, said quinacridone pigment having the following formula:



wherein R is selected from at least one member of the group consisting of CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OC<sub>2</sub>H<sub>5</sub>, and a halogen and R' is selected from at least one member of the group consisting of COOH, COOCa/2, SO<sub>3</sub>H, and SO<sub>3</sub>Ca/2, said layer having a thickness greater than about 10 microns, and exposing said charged plate to a pattern of activating electromagnetic radiation to produce an electrostatic latent image.

2. An electrophotographic imaging process which comprises uniformly charging the surface of an electrophotographic plate comprising a support substrate having a bulk conductivity greater than about 10<sup>8</sup> (ohms-centimeter)<sup>-1</sup>, having superimposed thereon a photoconductive layer comprising a photoconductive quinacridone pigment in a binder, said quinacridone pigment having the formula:



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wherein R is selected from at least one member of the group consisting of CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, OCH<sub>3</sub>, OC<sub>2</sub>H<sub>5</sub>, and a halogen and wherein R' is selected from at least one member of the group consisting of COOH, COOCa/2, SO<sub>3</sub>H, and SO<sub>3</sub>Ca/2, and selectively exposing said charged plate to activating electromagnetic radiation to produce an electrostatic latent image.

3. The process as disclosed in claim 1 further including the step of developing said latent image with electroscopic marking particles.

4. The process as disclosed in claim 2 further including the step of developing said latent image with electroscopic marking particles.

5. The process as disclosed in claim 3 wherein the imaging cycle of charging, exposing and developing is repeated at least once.

6. The process as disclosed in claim 4 wherein the imaging cycle of charging, exposing and developing is repeated at least one time.

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GEORGE F. LESMES, Primary Examiner

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U.S. Cl. X.R.

96—1.5; 117—17.5