United States Patent [19]

Byrne

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[45] **June 11, 1974**

[54] **ELECTROPHOTOGRAPHIC ELEMENT CONTAINING PHTHALOCYANINE**

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[22] Filed: **Jan. 3, 1966**

[21] Appl. No.: **518,450**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 375,191, June 15, 1964, abandoned.

[52] **U.S. Cl.** ..... **96/1.5,** 96/1 R, 96/1.2, 96/1.6, 101/462, 101/457

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

[58] **Field of Search** 96/1.5–1.8; 260/314.5, 88.3, 80.72, 41; 252/501

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[57] **ABSTRACT**

An electrophotographic plate comprising phthalocyanine pigment dispersed in a binder material is disclosed. Methods of preparing and using said plate in electrophotographic processes are also disclosed.

27 Claims, 2 Drawing Figures

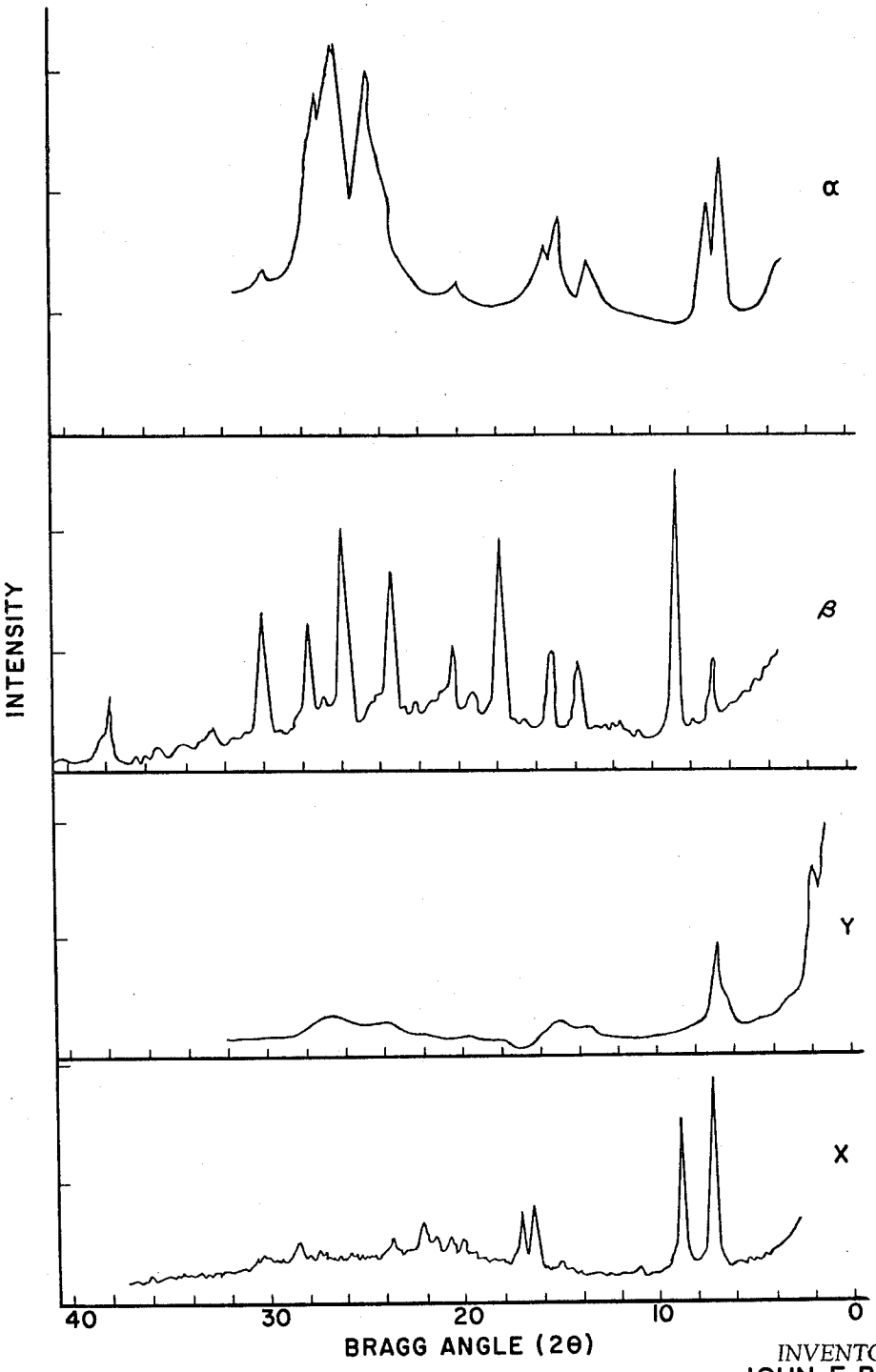

FIG. 1

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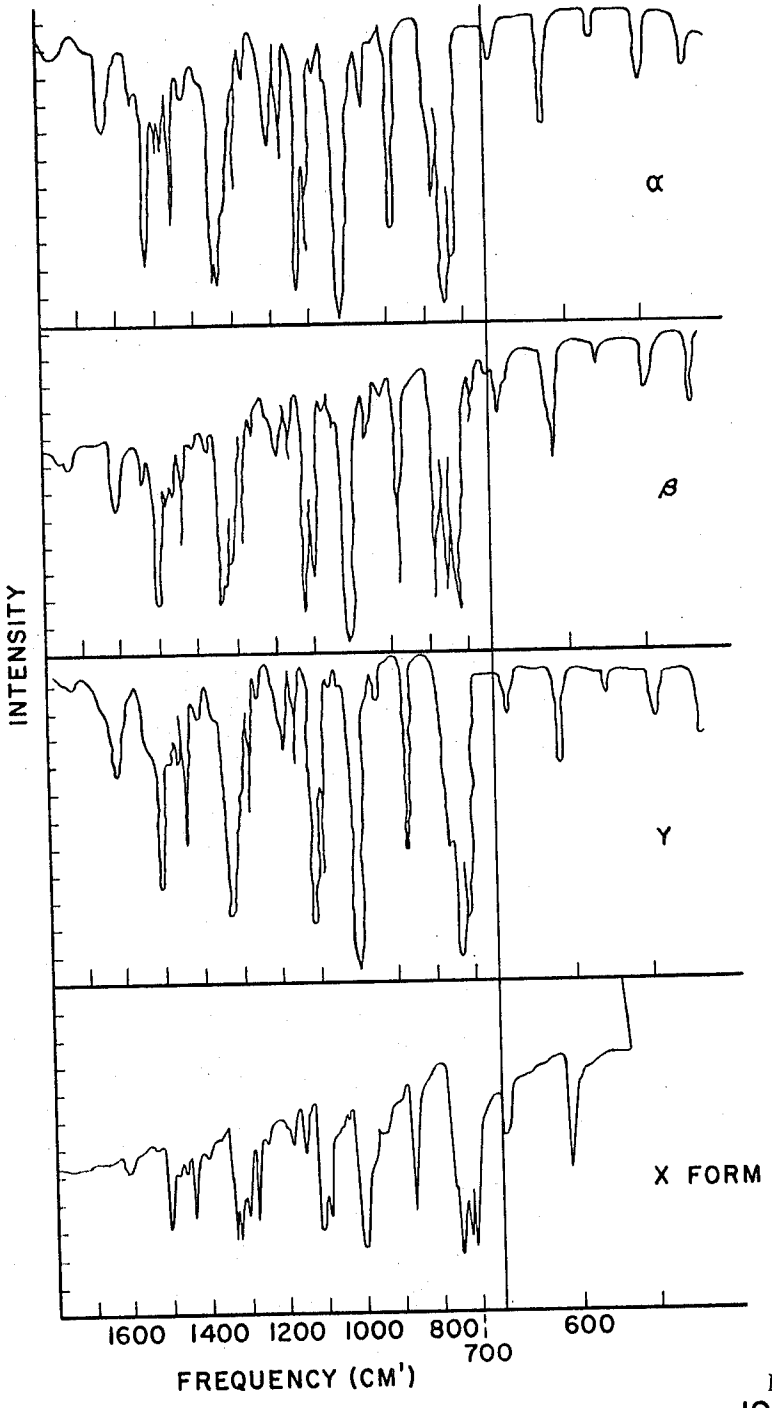

FIG. 2

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ELECTROPHOTOGRAPHIC ELEMENT CONTAINING PHTHALOCYANINE

This application is a continuation-in-part of parent application Ser. No. 375,191, filed in the United States Patent Office on June 15, 1964, now abandoned.

This invention relates to electrophotography and more particularly to a binder plate usable in xerography.

In the art of xerography as originally disclosed by Carlson in U.S. Pat. No. 2,297,691, an electrostatic latent image is formed on a photoconductive insulating layer and is developed thereon by finely divided electroscopic developing materials. The developed image may then be fixed in place or transferred to a copy sheet where it is permanently fixed. Generally the photoconductive insulating layer is first charged to sensitize it and is then exposed to a light image or other pattern of activated electromagnetic radiation to dissipate the charge in radiation struck areas. Thus the charge pattern formed conforms to the electromagnetic radiation pattern which impinges upon the plate. This charge pattern may then as above discussed be developed or made visible by a charge wise deposition on the plate of an electroscopic or electrostatically attractable, finely divided colored material which is referred to in the art as "toner."

As disclosed in the above noted Carlson patent, suitable inorganic and organic materials may be used to form the photoconductive insulating layer on which the latent electrostatic image is formed. Other photoconductive materials have been disclosed in the piror art as being useful in similar electrophotographic processes such as in U.S. Pat. Nos. 2,357,809; 2,891,001; and 3,079,342. Some of these materials are vitreous selenium, polymers such as polyvinylcarbazole, and resin suspensions of inorganic photoconductive pigments such as, for example, zinc oxide and cadmium sulfide. While most of these materials have evidenced some commercial utility, there are certain inherent disadvantages to the commercial use of each of the suggested compositions.

The discovery of the photoconductive insulating properties of highly purified vitreous selenium has resulted in this material becoming the standard in commercial xerography. Vitreous selenium, however, is sensitive only to wave lengths shorter than about 5,800 A. U. In addition, xerographic plates made with selenium are expensive to manufacture since this material must be applied to the supporting substrate by vacuum evaporation under carefully controlled conditions. Also, vitreous selenium layers are only meta-stable and may be re-crystallized into inoperative crystalline forms at temperatures only slightly in excess of those prevailing in conventional xerographic copying machines.

Other known xerographic plates made with certain aromatic organic photoconductors have relatively low sensitivity to light and have most of this sensitivity in the ultra-violet range, which is not fully satisfactory for use in conventional electrophotographic copying devices. Even the most sensitive organic photoconductive polymers leave much to be desired for commercial purposes. The choice of materials available for use in aromatic polymeric plates is of course limited because of the necessity of the selection of an already photoconductive material. In addition, all of the above noted xerographic plates lack abrasion resistance and stability of operation particularly at elevated temperatures.

Binder plates containing zinc oxide pigments, while comparatively inexpensive, are lower in sensitivity as compared with vitreous selenium plates and are not reusable. Also, as above noted, their visible sensitivity is quite limited. Furthermore, it is necessary to use such high percentages of photoconductive pigment in order to attain adequate sensitivity that it is difficult in zinc oxide plates to obtain smooth surfaces which lend themselves to efficient toner transfer and subsequent cleaning prior to reuse. An additional drawback in the use of zinc oxide binder type plates is that they can be sensitized only by negative and not by positive corona. This property makes them commercially undesirable since negative corona discharge generates much more ozone than positive corona discharge and is generally harder to control.

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

Another object of this invention is to provide electrophotographically reusable plates having sensitivities which extend over substantially the entire visible spectrum.

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

Yet another object of this invention is to provide a reusable xerographic plate which will produce images from colored originals having vastly improved contrast.

Yet a still further object of this invention is to provide a novel xerographic process wherein a reusable plate is utilized which has exceptional mechanical strength and hardness, high temperature and abrasion resistance under substantially normal conditions of xerographic machine operation.

Yet a further object of this invention is to provide highly sensitive panchromatic compositions which may be used in xerographic, xeroprinting, hydroprinting, heat deformable and lithographic processes.

Still a further object of this invention is to provide materials which may be used in the manufacture of flexible printing plates adapted for use in flexographic printing processes.

Still a further object of this invention is to provide a material suitable for use in the manufacture of reusable plates useful in color xerography and other electrophotographic processes.

Yet a still further object of this invention is to provide panchromatic xerographic plates of substantially high resolution for use in micro-printing and imaging applications.

The foregoing objects and others which will become apparent from the following description are accomplished in accordance with this invention, generally speaking, by providing a novel photoconductive layer containing a phthalocyanine in a film forming binder in a plate adapted for use in electrophotography. This photoconductive layer has particular utility in a xerographic process where reusability of the plate is desired. The phthalocyanine-binder photoconductive layer may be cast as a self-supporting film, or in lieu thereof may be deposited on any suitable supporting

substrate. The plate formed may be both with or without an overcoating on the photoconductive layer. AS a third alternative to the above noted self-supporting layer and substrate supported layer, the phthalocyanine-resin photoconductive layer may be used in the formation of multi-layer sandwich configuration xerographic plates.

It has been found in the present invention that suspensions of phthalocyanine pigments in insulating binders are not only capable of sustaining the very high fields required in commercial xerography, but are also highly photoconductive whether or not the binder itself is photoconductive. Since a wide variety of binders may be used in the present invention, including not only photoconductive materials but also varying for example, from soft thermoplastics to hard cross linked enamels, and since percentages of phthalocyanine required in these compositions are relatively low, the mechanical properties of the photoconductive layers are substantially determined by the properties of the binders. This is highly desirable since the selection of the photoconductive layer to be used may therefore be varied over a wide range by selection of the appropriate binder to suit the specific requirements of each particular situation. In this regard, these photoconductive layers are substantially different from the heretofore known binder suspensions of inorganic pigments which require such a high percentage of inorganic pigment that the inorganic pigment used essentially controls the physical properties of the final photoconductive layer.

The binder may itself be a photoconductive material or contain a photoconductive material blended into it. Other organic or inorganic photoconductive pigments may also be dispersed in the binder along with the phthalocyanine regardless of the photoconductivity of the binder.

When it is desired to coat the phthalocyanine-binder film on a substrate, various supporting materials may be used. Suitable materials for this purpose are aluminum, steel, brass, metallized or tin oxide coated glass, semi-conductive plastics, and resins, paper and any other convenient material. Any suitable dielectric material may be used to overcoat the photoconductive layer. A typical overcoating is bichromated shellac.

Any suitable phthalocyanine may be used to prepare the photoconductive layer of the present invention. The phthalocyanine used may be in any suitable crystal form. It may be substituted or unsubstituted both in the ring and straight chain portions. Reference is made to a book entitled "Phthalocyanine Compounds" by F. H. Moser and A. L. Thomas, published by the Reinhold Publishing Company, 1963 edition for a detailed description of pththalocyanines and their synthesis. Any suitable phthalocyanine may be used in the present invention. Phthaloycanines encompassed within this invention may be described as compositions having four isoindole groups linked by four nitrogen atoms in such a manner so as to form a conjugated chain, said compositions have the general formula $(C_8H_4N_2)_4R_n$ wherein R is selected from the group consisting of hydrogen, deuterium, lithium, sodium, potassium, copper, silver, beryllium, magnesium, calcium, zinc, cadmium, barium, mercury, aluminum, gallium, indium, lanthanum, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, titanium, tin, hafnium, lead, silicon, gervanium, thorium, vanadium, antimony, chromium, molybdenum, uranium, manganese, iron, cobalt, nickel, rhodium, palladium, osmium, and platinum; and n is a value of greater than 0 and equal to or less than 2. Any other suitable phthalocyanines such as ring or aliphatically substituted metallic and/or non-metallic phthalocyanines may also be used if suitable. As above noted, any suitable phthalocyanine may be used to prepare the photoconductive layer of the present invention. Typical phthalocyanines are: aluminum phthalocyanine, aluminum polychlorophthalocyanine, antimony phthalocyanine, barium phthalocyanine, beryllium phthalocyanine, cadmium hexadecachlorophthalocyanine, cadmium phthalocyanine, calcium phthalocyanine, cerium phthalocyanine, chromium phthalocyanine, cobalt phthalocyanine, cobalt chlorophthalocyanine, copper 4-aminophthalocyanine, copper bromochlorophthalocyanine, copper 4-chlorophthalocyanine, copper 4-nitrophthalocyanine, copper phthalocyanine, copper phthalocyanine sulfonate, copper polychlorophthalocyanine, deuteriophthalocyanine, dysprosium phthalocyanine, erbium phthalocyanine, europium phthalocyanine, gadolinium phthalocyanine, gallium phthalocyanine, germanium phthalocyanine, hafnium, phthalocyanine, halogen substituted phthalocyanine, holmium phthalocyanine, indium phthalocyanine, iron phthalocyanine, iron polyhalophthalocyanine, lanthanum phthalocyanine, lead phthalocyanine, lead polychlorophthalocyanine, cobalt hexaphenylphthalocyanine, copper pentaphenylphthalocyanine, lithium phthalocyanine, lutecium phthalocyanine, magnesium phthalocyanine, manganese phthalocyanine, mercury phthalocyanine, molybdenum phthalocyanine, naphthalocyanine, neodymium phthalocyanine, nickel phthalocyanine, nickel polyhalophthalocyanine, osmium phthalocyanine, palladium phthalocyanine, palladium chlorophthalocyanine, alkoxyphthalocyanine, alkylaminophthalocyanine, alkylmercaptophthalocyanine, aralkylaminophthalocyanine, aryloxyphthalocyanine, arylmercaptophthalocyanine, copper phthalocyanine piperidine, cycloalkylaminophthalocyanine, dialkylaminophthalocyanine, diaralkylaminophthalocyanine, dicycloalkylaminophthalocyanine, hexadecahydrophthalocyanine, imidomethylphthalocyanine, 1,2 naphthalocyanine, 2,3 naphthalocyanine, octaaxaphthalocyanine, sulfur phthalocyanine, tetraazaphthalocyanine, tetra-4-acetylaminophthalocyanine, tetra-4-aminobenzoylphthalocyanine, tetra-4-aminophthalocyanine, tetrachloromethylphthalocyanine, tetradiazophthalocyanine, tetra-4,4-dimethyloctaazaphthalocyanine, tetra-4,5-diphenylenedioxide phthalocyanine, tetra-4,5-diphenyloctaazaphthalocyanine, tetra-(6-methylbenzothiazoyl) phthalocyanine, tetra-p-methylphenylaminophthalocyanine, tetramethylphthalocyanine, tetra-naphthotriazolylphthalocyanine, tetra-4-naphthylphthalocyanine, tetra-4-nitrophthalocyanine, tetra-peri-naphthylene-4,5-octaazaphthalocyanine, tetra-2,3-phenyleneoxide phthalocyanine, tetra-4-phenyloctaazaphthalocyanine, tetraphenylphthalocyanine, tetraphenylphthalocyanine tetracarboxylic acid, tetraphenylphthalocyanine tetrabarium carboxylate, tetraphenylphthalocyanine tetra-calcium carboxylate, tetrapyridyphthalocyanine, tetra-4-trifluoromethylmercaptophthalocyanine, tetra-4-trifluoromethylphthalocyanine, 4,5-thionaphthene-

octaazaphthalocyanine, platinum phthalocyanine, potassium phthalocyanine, rhodium phthalocyane, samarium phthalocyanine, silver phthalocyanine, silicone phthalocyanine, sodium phthalocyanine, sulfonated phthalocyanine, thorium phthalocyanine, thulium phthalocyanine, tin chlorophthalocyanine, tin phthalocyanine, titanium phthalocyanine, urnaium phthalocyanine, vanadium phthalocyanine, ytterbium phthalocyanine, zinc chlorophthalocyanine, zinc phthalocyanine, others described in the Moser text and mixtures, dimers, trimers, oligomers, polymers, copolymers or mixtures thereof.

Any suitable insulating, film forming binder whether organic or inorganic may be used in combination with the phthalocyanine to prepare the photoconductive layer of this invention. In order to be useful, the binder used in the present invention must be more resistive than about 10^{10} and preferably more than 10^{12} ohm/cm. under the conditions of xerographic use. It is to be understood that the term "insulating" as used here includes both photoconductive insulating material and conventional insulators which are substantially nonresponsive to light exposure. Typical photoconductive insulating materials include films of amorphous selenium, sulfur, sulfur-selenium mixtures, arsenic-selenium mixtures, selenium-tellurium mixtures, lead oxide, cadmium sulfide, zinc sulfide and organic photoconductors (especially when these are complexed with small amounts of suitable Lewis acids). Typical of these organic photoconductors are polyvinylcarbazole; polyvinylanthracene; 4,5-diphenylimidazolidinone; 4,-5-diphenylimidazolidinethione; 4,5-bis-(4'-aminophenyl)-imidazolidinone; 1,5-cyanonaphthalene; 1,4-dicyanonaphthalene; aminophthalodinitrile; nitrophthalidinitrile; 1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8); 3,4-di(4'-methoxy-phenyl)-7,8-diphenyl-1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8); 3,4-di-(4'-phenoxy-phenyl-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8); 3,4,7,8-tetramethoxy-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8); 2-mercaptobenzthiazole; 2-phenyl-4-diphenylidene-oxazolone; 2-phenyl-4-p-methoxy-benzylidene-oxazolone; 6-hydroxy-2-phenyl-3-(p-dimethylamino phenyl)-benzofuran; 6-hydroxy-2,3-di(p-methoxy-phenyl)-benzofuran; 4-dimethylaminobenzylidene-benzhydrazide; 4-dimethylaminobenzylideneisonicotinic acid hydrazide; furfurylidene-(2)-4'-dimethylamino-benzhydrazide; 5-benzilideneamino-acenaphthene; 3-benzylideneamino-carbazole; (4-N,N-dimethylamino-benzylidene)-p-N,N-dimethylaminoaniline; (2-nitro-benzylidene)-p-bromo-aniline; N,N-dimethyl-N'-(2-nitro-4-cyano-benzylidene)-p-phenylene-diamine; 2,4-diphenyl-quinazoline; 2-(4'-amino-phenyl)-4-phenyl-quinazoline; 2-phenyl-4-(4'-dimethyl-amino-phenyl)-7-methoxy-quinazoline; 1,3-diphenyl-tetrahydroimidazole; 1,3-di(4'-chlorophenyl)-tetrahydroimidazole; 1,3-diphenyl-2-4'-dimethyl amino phenyl)-tetrahydroimidazole; 1,3-di-(p-tolyl)-2-quinolyl-(2'- -tetrahydroimidazole; 3-(4'-dimethylamino-phenyl)-5-(4''-methoxyphenyl-6-phenyl-1,2,4-triazine; 3-pyridil-(4'')-5-(4''-dimethylamino-phenyl)-6-phenyl-1,2,4-triazine; 3,(4'-amino-phenyl)-5,6-di-phenyl-1,2,4-triazine; 2,5-bis 4'-amino-phenyl-(1') -1,3,4-triazole; 2,5-bis 4'-(N-ethyl-N-acetyl-amino)-amino)-phenyl-(1') -1,3,4-triazole; 1,5-diphenyl-3-methyl-pyrazoline; 1,3,4,5-tetraphenyl-pyrazoline; 1-methyl-2-(3'4'-dihydroxymethylene-phenyl)-benzimidazole; 2-(4'-dimethylamino phenyl(-benzoxazole; 2-(4'-methoxyphenyl)-benzthiazole; 2,5-bis- p-aminophenyl-(1) -1,3,4-oxadiazole; 4,5-diphenylimidazolone; 3-aminocarbazole; copolymers and mixtures thereof. Typical insulating film forming binders include thermoplastic and thermoset polymers such as polyvinylchloride, polyvinylacetates, polystyrene, polystyrene-polybutadiene copolymer, polymethacrylates, polyacrylics, polyacrylonitriles, silicone resins, chlorinated rubber, epoxy resins including halogenated epoxy and phenoxy resins, phenolics, epoxy-phenolic copolymers, epoxy urea formaldehyde copolymers, epoxy melamine formaldehyde, polycarbonates, polyurethanes, polyamides, saturated polyesters, unsaturated polyesters cross-linked with vinyl monomers and epoxy esters, vinyl epoxy resins, tall-oil modified epoxys, and copolymers and mixtures thereof. Other insulating film-forming binder materials include organics such as sucrose and its derivates, rosin and modified rosins etc; inorganic materials such as low melting point insulating glasses including those made from glass-forming oxides, sulfides, selenides, borates, phosphates, arsenates, other well known glass formers and mixtures thereof. In addition to the above noted materials, any other suitable binder may be used if desired.

The phthalocyanine pigments may be incorporated in the dissolved or melted binder by any suitable means such as strong shear agitation, preferably with simultaneous grinding. These methods include ball milling, roller milling, sand milling, ultrasonic agitation, high speed blending and any desirable combination of these methods. In addition to adding the phthalocyanine pigment to the dissolved or melted binder material it may also be added and blended into a dry or slurried form of the powdered binder material before it is heated or dissolved to make it film forming. Any suitable range of pigment-resin ratio may be used; on a phthalocyanine pigment-dried binder weight basis, this range extends from about 1/1 to about 1/100 while the preferred range extends from about ¼ to about 1/15. Optimum results are obtained when ratios from about 1/6 to about 1/12 are used and accordingly this range is most preferred. It should be noted in this regard that the preferred range of components lies substantially below that used in making heretofore known inorganic photoconductor-binder plates which are generally quite unsatisfactory in sensitivity when the pigment-binder ratio drops below about 2/1. Other photoconductive pigments may also be added to they system when phthalocyanine is used in the ratios given above.

The ability in the present invention to use lower pigment to binder ratios represents a highly desirable advantage over the prior art since a smaller proportion of the relatively expensive organic pigment component is required permitting very smooth adhesive coatings to be obtained because of the high binder content. A much wider latitude of material is also accomplished by the present invention since the physical properties of the plates may be determined substantially by selection of the binder; because the physical properties are little affected by the presence of the pigment. Thus, one may choose binders having the desired softening range, smoothness, hardness, toughness, solvent resistance, or solubility, water repellency photoconductivity and the

like with assurance that the pigment will not affect these properties to any considerable extent.

The pigment-binder-solvent slurry (or the pigment-binder-melt) may be applied to conductive substrates by any of the well-known painting or coating methods, including spray, flow coating, knife-coating, electrocoating, Mayer bar drawdown, dip coating, reverse roll coating, etc. Spraying in an electric field may be preferred for smoothest finish and dip coating 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 used for other painting applications. For example, phthalocyanine-epoxy plates may be cured by adding a cross-linking agent and stoving according to approximately the same schedule as other baking enamels made with the same resins, and similar pigments for paint applications. A very desirable aspect of the phthalocyanine pigments 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, similar to automotive or kitchen appliance resin and glass enamels.

The thickness of the phthalocyanine films may be varied from about 1 to hundreds of microns, depending on the required individual needs. Self-supporting films, for example, cannot usually be manufactured in thicknesses 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 in the 5 to 80 micron range for most uses. For certain compositions and purposes it is desirable to provide an overcoating; this should usually not exceed the thickness of the photoconductive coating, and preferably not above ¼ of the latter. Any suitable overcoating material may be used such as bichromated shellac. A series of detailed examples indicating our preferred procedure of making the plate by mixing, milling, coating and the like is presented below.

While any suitable phthalocyanine or mixtures of phthalocyanines may be used in the present invention, it has been found that for best results in xerographic processes, a non-substituted metal-free phthalocyanine is much preferred over the others. As above noted, phthalocyanines useful in the present invention include all the crystal forms of metal-free phthalocyanines such as alpha, beta, and what is hereinafter referred to as the "X" form of phthalocyanine. The exact physical structure of the X crystalline form phthalocyanine is not presently understood, however it is recognized as being different from the alpha, beta and gamma forms by its distinct x-ray diffraction pattern and its infrared spectrum.

The diffraction pattern and the spectrum are indicated in attached FIGS. **1** and **2**, respectively.

Referring now to FIG. **1**, there is seen four x-ray diffraction curves in vertical alignment for easy comparison. The uppermost curve is for alpha form, the second is for beta form, the third is for gamma form and the fourth is an experimental curve for X-form. The curves for alpha, beta and gamma forms are taken from C. Hamann and M. Starke, "Investigation of the Electrical and Thermo-electric Properties of the Modification of Metal-free Phthalocyanine," Phys. stat. Vol. 4, 509 (1964). As can be seen from FIG. **1**, it is not possible to make a clear cut distinction between alpha and gamma forms. Gamma form may merely be a highly amorphous modification of alpha phthalocyanine. However, the curve for X-form may be easily distinguished. As seen in FIG. **1**, the spectra for X-form has peaks at Bragg angles of about 17.3 and 22.3 which exist in none of the α, β and γ polymorph spectra. Also, the peak at about 9.1 in the X-form spectra is not present in the spectra of α and γ forms. Major peaks for X-form fall at Bragg angles of about 7.5, 9.1, 16.7, 17.3 and 22.3. All X-ray measurements were made with Copper K radiation having a wavelength of 1.54050 Angstrom Units.

FIG. **2** shows a comparison between an experimentally obtained infrared spectra for X-form metal-free phthalocyanine and infrared spectra for alpha, beta and gamma metal-free phthalocyanine obtained from the literature. These curves are arranged in vertical alignment for easy comparison. These curves are conventional infrared spectra, plotting intensity against frequency in cm^{-1}. The spectra for alpha, beta and gamma phthalocyanine are taken from the Hamann and Starke article cited above. Again, it can be seen that there is very little, if any, difference between alpha and gamma phthalocyanine. This strengthens the hypothesis that gamma phthalocyanine is merely a more amorphous form of alpha phthalocyanine. The infrared spectra for X-form can be easily distinguished from the reported spectra for alpha, beta and gamma forms. The variation in peak intensity and location for the different polymorphic forms is expecially noticeable in the 700–800 cm^{-1} and 1250–1350 cm^{-1} regions.

Specific preparations of the alpha, beta and X forms of phthalocyanine are as follows.

Preparation of Alpha Metal-Free Phthalocyanine

Lithium phthalocyanine, 86.7 g. is added to 600 ml. of well stirred concentrated sulfuric acid at 0°C. The mixture is then stirred at this temperature for 2 hours. The resultant solution is then filtered through a coarse sintered glass funnel and poured slowly and with stirring into 4 liters of ice and water. After sitting for several hours, the mixture is filtered and the cake is washed to neutrality with water. The cake is then finally rinsed with methanol several times and dried in air. The resultant powder is then extracted with acetone in a continuous extraction unit for 24 hours and allowed to dry in air to give a blue powder.

To insure against lithium salt residues, the precipitation is repeated. Thus, there is produced 55.4 g. of a blue powder whose x-ray pattern matched that of the known published pattern for alpha metal-free phthalocyanine.

Preparation of Beta-Free Phthalocyanine

A 10 g. supply of commercial Monolite Fast Blue GS is placed in a vycor dish which is then inserted in a 2-inch glass tube suitable for heating in a combustion tube furnace. The temperature of the furnace is raised slowly to 350°C. during the first 1½ hours to avoid scattering of sample, and finally maintained at 350 – 430°C. during the next 4 hours. A stream of dry nitrogen is passed through the tube throughout the heat treatment. The treated sample is transferred to a desiccator for cooling, whereupon 9.45 g. of blue-black powder that gives an x-ray pattern consistent with that of the Beta-form is obtained.

Preparation of X Form Metal-Free Phthalocyanine

A 9 g. sample of alpha metal-free phthalocyanine prepared by precipitation from sulfuric acid solution,

and 90 g. of sodium chloride is placed in a quart-size porcelain ball mill and rolled at about 70 rpm for 72 hours.

The ground powder is removed manually from the mill and extracted with 1500 ml. of 1 percent hydrochloric acid at 70 – 80°C. for 1 hour. The resultant slurry is filtered and the cake is washed repeatedly with distilled water to remove the remaining sodium chloride. The cake is finally rinsed with methanol several times and dried in air to give 8.8 g. of blue powder. The x-ray diffraction pattern of this material cannot be reconciled with any of the patterns published for the various polymorphic forms of metal-free phthalocyanine and agrees with the patterns assigned to X-form as shown in FIGS. I and II. Hence it is designated as the X form of metal-free phthalocyanine.

While the most effective plates are made by incorporation of the X form of metal-free pigment in resin binders, very good plates are also made with the alpha metal-free form, particularly when this is converted to either the beta by solvent recrystallization or X form in a coating as will be described below. In order to identify the crystal form of the phthalocyanine pigment as it actually exists in the photoconductive layer after the photoconductive layer is dried and cured, the photoconductive coating is scraped off its substrate and powdered without any attempt to remove the surrounding resin (the latter does not seriously interfere with the measurement.) It is then filled into a capillary and various experiments are run on compressed powder pellets. The results of these experiments are recorded as above described in FIG. 1 (on alpha, beta, gamma and X form metal-free phthalocyanine pigments) in comparison with those of the literature.

Infrared measurements can be applied only to pigments without resin matrix because, of course, the resin absorption interferes and masks that of the pigment. The phthalocyanine pigment was suspended in a Nujol mull and subsequently examined in a standard infrared spectrophotometer (Perkin-Elmer Infracord Model No. 137). FIG. II shows the infrared spectra of these alpha, beta, gamma and X form metal-free pigments.

One type of transformation of crystal forms resulted in dramatic changes in crystal size and shape that could readily be observed under the microscope while it was happening. This is the recrystallization of unstabilized alpha metal-free phthalocyanine to beta metal-free phthalocyanine in a resin coating (VYNS and Epidene) which is treated by a suitable solvent vapor. The alpha pigment in the original coating is deep blue, finely dispersed as amorphous appearing particles smaller than about 10 microns. Upon treatment for from about 5 to 15 minutes with hot vapors (at about from 170 – 180° of, for example, anthracene or phthalic anhydride, the color changes dramatically to a blue-green in the treated areas. Simultaneously the crystallites grow into interconnected stacks of fine needles which may be identified as nearly pure beta form of the pigment. The array of needles appears under the microscope like a loosely matted pile of straw. The observed enhancement in photosensitivity may possibly be accounted for by the network of needles whose random arrangement present many points of near contact throughout the thickness of the coating. The crystal change before and after recrystallization is apparent by microscopic examination.

While it is possible to make operable plates using commercial grade phthalocyanine pigments, such as Monolite Fast Blue GS (Arnold Hoffman Co., Division of ICI Limited), Heliogen Blue G (General Aniline Film Corporation), or Cyan Green 15-3100 (American Cyanamid Corporation), the purity control ordinarily exercised in the manufacture of these paint, ink and resin colorants is inadequate for large scale commercially reliable performance in xerographic devices. When commercial grade pigments are to be used, it is therefore desirable to purify them by known procedures, such as solvent washing of the pigments, and subsequent solution in concentrated sulfuric acid followed by precipitation in ice-cold water. Various solvents can be used such as ketones, alcohols, or chlorinated hydrocarbons. When such purification procedures were applied to typical commercial batches of, for example, Monolite Fast Blue GS, the photosensitivity of the resulting plates was increased by about 4 to 6 fold over unpurified controls and reached a more or less consistent value.

Still better results are obtained by special synthesis of pigments for use in xerographic applications. The synthesis methods used are well known and are listed below with reference to the published literature, each process is discussed in "Phthalocyanine Compounds" below cited.

A. Metal-Free Phthalocyanine

1. Alpha metal-free phthalocyanine was prepared by each of the following synthesis routes:
   a. methanolysis of dilithium phthalocyanine
   b. acid hydrolysis of dilithium phthalocyanine, with optional reprecipitation from sulfuric acid.

2. Beta metal-free phthalocyanine was prepared from alpha form phthalocyanine by extended heating of the dry powder or by prolonged agitation in an aromatic solvent. Details of the preferred procedure are presented below.

3. Gamma metal-free phthalocyanine was prepared from calcium phthalocyanine by acid hydrolysis, according to *Phthalocyanine Compounds*, by Frank H. Moser and Arthur C. Thomas, 1963 edition, published by Reinhold Publishing Corp.

4. X form metal-free phthalocyanine was prepared from alpha metal-free phthalocyanine by extended ball milling in salt particles followed by desalting.

B. Metal Phthalocyanines

The following metal phthalocyanine complexes were used to make xerographic plates. These gave images which were generally inferior in contrast and photosensitivity to those obtained with metal-free phthalocyanine in comparable binders;

Chlorinated Copper phthalocyanine
Beta Copper phthalocyanine
Lead phthalocyanine
Zinc phthalocyanine

It was noticed that the performance of these materials in part was a function of the binder used, for example copper phthalocyanine and chlorinated copper phthalocyanine which were comparatively inferior in a vinyl resin (VYNS-3 vinyl chloride-vinyl acetate copolymer) gave an acceptable image in a silicone binder (SR-82 dimethyl polysiloxane).

In the disclosure various tradenames will be used to define specific binders and phthalocyanines. The following is a list of components identified in the ensuing

disclosure identifying the basic chemical structure of each:

RESINS:

Oxiron 2002 — is an epoxidized polyolefin made by the FMC Corporation;

VYNS-3 — is a polyvinyl chloride-acetate copolymer made by Union Carbide Corporation;

Epidene 168/50 — is a tall oil modified epoxy resin made by T. F. Washburn Company;

SR-82 — is a silicone resin made by the General Electric Company;

Acryloid B-72 — is a polyacrylate made by Rohm & Haas Company;

Lucite 44 and 46 are polymethacrylates made by the DuPont Company;

PS-2 — is a polystyrene resin made by the Pennsylvania Industrial Chemical Company;

Nitrocellulose made by the Hercules Powder Company;

Pliolite S-7 — is a polystyrene-butadiene copolymer made by the B. F. Goodrich Company;

Araldite 571-K and 6040 are epoxy resins made by the Ciba Chemical Company;

Eponol 55-B-40 — is a phenoxy resin made by the Shell Chemical Company;

DC Silicone R-5061 — is a silicone resin made by the Dow Corning Company;

Geon 222 — is a vinyl acetate-vinyl chloride copolymer made by the Goodyear Chemical Company;

RMD 4511 — is a styrene acrylonitrile copolymer made by the Union Carbide Corporation;

Parlon — is a chlorinated rubber made by the Hercules Powder Company;

Pliolite S-5, VT, VTL, VTLNX — are all vinyl toluene polymers made by the Goodyear Chemical Company;

Vinac B-100 — is a vinyl acetate resin made by Air Reduction Company;

Tygon TP-107-B — is an unpigmented metal primer made of a thermoplastic resin made and sold by U.S. Stoneware Company:

VMCH — is a maleic acid modified acetate-vinyl chloride copolymer made by the Union Carbide Corporation;

Synthetasine 200 — is a thermosetting resin made by the Interchemical Corporation;

DER 542 — is a brominated epoxy resin made by the Dow Chemical Corporation.

The phthalocyanines used throughout this disclosure are identified as Monolite Fast Blue GS — which is a mixture of alpha and beta metal-free phthalocyanine made by the Arnold Hoffman Company which is a Division of ICI, Ltd.; Heliogen Blue G — is a metal-free phthalocyanine; Heliogen Blue BGN is a copper phthalocyanine; Heliogen Green B, Heliogen Green and Heliogen Green RT are all chlorinated copper phthalocyanines made by General Aniline and Film; Cyan Green 15-3100 is a chlorinated copper phthalocyanine made by American Cyanamid.

It was pointed out above that certain crystal forms of the preferred pigment (metal-free phthalocyanine) are more light sensitive than others. Observations indicate that consistently the best plates are obtained if one starts with the stabilized X form of metal-free phthalocyanine and coats, dries and cures the plates under conditions in which this modification is preserved without substantial recrystallization. The next best procedure is to start with alpha form pigment, and coat, dry and cure under conditions under which at least some of the alpha recrystallizes to either the X or beta form in the coating. In fact, a novel solvent vapor treatment as will be described below has been accomplished to achieve the transformation to the beta form deliberately. In another preferred embodiment plates are prepared from the alpha form of the pigment without recrystallization during or after coating. Comparatively poorer results were obtained in plates prepared solely from the beta modification of the pigment.

In summary, all crystal forms of metal-free phthalocyanines are desirable for the present intended use, but the X form pigment is the preferred material for simple, economical manufacturing of xerographic plates of high sensitivity and excellent reusability.

The recrystallization of alpha form phthalocyanines to the beta form in coating mixtures or in pre-existing coatings may be carried out by:

1. Inclusion of about 25 percent by volume of the high boiling recrystallizing solvent in the coating mixture, and heating the plate during the last stages of drying and curing. A number of solvents, which have been found to be suitable for this approach, particularly for use with thermoplastic binder resins include benzyl benzoate, benzylether, dibenzylketone, N-methyl-N-phenylbenzamide, quinoline, alpha,2,4-trichlorotoluene, and suitable mixtures thereof.
2. Treatment of the dried coating with hot vapor of a recrystallizing agent. In the laboratory this may be achieved by placing the air dried resin plate face down over an evaporating dish containing the recrystallizing agent and subliming in an oven the latter compound onto the plate for about 5 to 15 minutes. After the vapor treatment the recrystallizing agent and residual solvent are driven off by the baking until no residues can be detected by appropriate analytical procedures such as vapor chromatography.

The following agents for examples are effective, particularly for use on the thermoplastic vinyl resin plates: Acenaphthene, acridine, anthracene, benzophenone, phthalic anhydride, naphthalene, biphenyl, and mixtures thereof.

The specific phthalocyanine plates above defined have utility in either reusable and/or single xerographic systems. The reusability of the photoconductive layer of the present invention was established by a procedure which can generally be described as follows.

The xerographic plate containing the phthalocyanine resin photoconductive layer was charged, imaged and cascaded in commercial xerographic apparatus described as Xerox Number 1 Camera and using a Xerox Flat Plate apparatus. The developer used was a commercially available xerographic developer such as is described in U.S. Pat. Nos. 2,788,288; Re 25,136; and 3,079,342. The toner image was electrostatically transferred to paper, the residual toner was released and wiped off in the normal fashion. The plates were then at least twice cylically re-charged, re-electrometered, re-exposed, and developed.

A wide variety of phthalocyanine plates in the preferred composition range were found to give reproducible electrometer reading and image properties. With organic resin binders plates beyond the high end of the

pigment/resin ratio range were found to give progressively decreasing charge acceptance.

Other plates were developed by means of liquid developers, by means of aqueous pigment suspension, aerosol powders and frost deformation. The photoconductive layers were satisfactorily reusable in many cases. It was found that the reusability could be improved in some cases by interposition of an extra charging step and blanket exposure between the final cleaning step of the proceeding imaging cycle and the initial charging step of the next period. The reason for this observation is not completely understood. Reusability, particularly of highly pigmented coatings may be improved also by overcoating with a thin dielectric layer.

The invention will be further described with reference to the following examples, which describe in detail various preferred embodiments of the present invention. Parts, ratios and percentages are by weight unless otherwise stated.

All the materials tested below are charged, exposed and developed in the conventional xerographic method and produce images ranging in quality. These images are designated in comparative terms in the ensuing examples. Very good images are designated by the symbol "A", good images are designated "B", fair images "C" and weak images "D".

EXAMPLES 1–7

An electrophotographic plate is prepared by initially mixing six grams of Oxiron 2002 (an epoxidized polyolefin) and one gram X-form metal-free phthalocyanine (made by the process above described). This mixture is formulated together with 3.5 grams phthalic anhydride, 9 grams n-butanol and 15 grams of acetone. The above mixture is milled for about eight hours with porcelain pebbles in a 6-ounce mixing vessel. To form the plates the resulting mixture is deposited on a bright finish 5 ml. aluminum foil with a No. 40 drawdown rod. The coating is cured for about 60 minutes at about 175°C.

Seven plates containing the photoconductive layer above defined are prepared for subsequent testings as indicated in the following table. It should be noted that each of the plates prepared contain the photoconductive layer without an overcoating. The seven plates are tested for positive charge acceptance (one pass under the corotron at 8.7 KV) and charge retention after exposure to 3-foot candle seconds of photoflood illumination. Results are as follows:

Plate Number	Charge Acceptance Volts	Charge Retention Volts — After Exposure	Image Quality
1	580	10	A
2	630	10	A
3	630	10	A
4	620	10	A
5	610	10	A
6	670	10	A
7	630	10	A

There was substantially little charge reduction or dark decay in unexposed areas. The reusability of the plates above tested was substantially enhanced by the addition of an overcoating to these plates.

General Preparation of Xerographic Plates Used in Examples 8 – 128

Mixtures using the specific phthalocyanine-resin binder are prepared by ball milling the phthalocyanine pigment in a solution of a resinous binder and one or more solvents until the pigment is well dispersed. The desired parts of phthalocyanine are added to the desired parts of resin solution in a suitable mixing vessel. Porcelain pebbles are added until the liquid just covers the pebbles. Milling is on rolls which are run at such speeds that the jar moves at about 80 r.p.m. Approximately 8 hours milling is required to achieve good dispersions of those phthalocyanines which are dispersed by this procedure and use any phthalocyanine to resin ratios of about 1 to 100. The milled mixture may be stored prior to decomposition on the supporting substrate.

Aluminum foils are used as the supporting substrate and the finsihed coatings are obtained by applying the coating mixture to the foil, flowing it back and forth and then allowing it to drain by gravity from the plate suspended so that the plane is essentially vertical or are coated with a drawdown rod. The coated plate is allowed to air dry and then is ready for precharge processing which may be merely heat curing the resin or may involve a recrystallization step. The recrystallizing agent may be sublimed up onto the coated plate to recrystallize in situ or be added to the coating mixture before coating on the aluminum foil.

EXAMPLES 8–10

The phthalocyanine used in these examples is Monolite Fast Blue GS in varying degrees of purity; the plate is made by the method described above. The following results are obtained using this Monolite with VYNS-3 as the film forming resin.

Phthalocyanine	Resin: Phthalocyanine Weight Ratio	Charge Acceptance Volts	Charge Acceptance Volts	Image Quality
Monolite Fast Blue GS	6:1	150	75	C
Monolite Fast Blue GS (acetone extracted)	6:1	240	55	B
Monolite Fast Blue GS (acetone extracted and acid precipitated)	6:1	265	13	A

The acetone treatment of the Monolite removes organic soluble non-phthalocyanine residual impurities.

The acid (sulfuric) treatment removes at least some of the inorganic impurities and converts the phthalocyanine to the alpha form.

EXAMPLES 11–16

The resin to phthalocyanine weight ratio used is of significant importance in obtaining desirable results. The variation in results is illustrated by the below runs where the same components are used in varying amounts. Epidene 168/50 and Monolite Fast Blue GS are used to make the photoconductive layer in all the plates tested; the results are as follows:

Resin: Phthalocyanine Weight Ratio	Charge Acceptance Volts	Charge Retention Volts	Image Quality
100:1	660	560	D
50:1	630	170	C
25:1	530	60	B
19:1	650	30	A
10:1	460	23	A
4:1	300	5	A

EXAMPLES 17–28

The phthalocyanines used in these examples are all metal phthalocyanines which may be made by methods described in J. Chem. Soc. (1936) 1719–1736. The plates are made by the method indicated above, and upon testing give the following results:

Phthalo-Cyanine	Film Forming Resin	Resin: Phthalo-Cyanine Weight Ratio	Charge Acceptance Volts	Charge Retention After Exposure Volts	Image Quality
Heliogen Blue-BGN	VYNS-3	9:1	90	50	C
Heliogen Green-B	SR-82	48:1	not available	not available	C
Heliogen Green-B	VYNS-3	9:1	70	50	D
Heliogen Green-RT	SR-82	48:1	860	500	B
Heliogen Green-Toner 66-3001	SR-82	48:1	1000	900	C
Heliogen Green-Toner 66-3001	VYNS-3	9:1	100	70	D
Aluminum	VYNS-3	6:1	50	40	D
Lead	VYNS-3	6:1	80	75	D
Copper Hexa-decabromo	VYNS-3	6:1	120	80	D
Copper Hexa-decachloro	SR-82	60:1	1100	900	D
Copper	VYNS-3	6:1	300	240	D
Cyan Green Toner 15-3100	SR-82	48:1	500	275	C

EXAMPLES 29–44

Metal-free phthalocyanines in a variety of resin binders are used to produce a xerographic image. Exceptionally good image quality is obtained with these metal-free phthalocyanines. The results are indicated below:

Phthalo-Cyanines	Resin	Resin to Phthalo-Cyanine Weight Ratio	Charge Accept-ance Volts	Charge Retention Volts-After Exposure	Image Quality
X-form	epoxy-phenolic	6:1	450	20	A
*Alpha to X-form	epoxy-phenolic	6:1	480	25	A
**Alpha to beta form	epoxy-phenolic	6:1	520	15	A
X-form	epoxidized polyolefin	6:1	630	10	A

Phthalo-Cyanines	Resin	Resin to Phthalo-Cyanine Weight Ratio	Charge Accept-ance Volts	Charge Retention Volts-After Exposure	Image Quality
*Alpha to X-form	epoxidized polyolefin	6:1	360	5	A
X-form	phenolic	6:1	550	10	A
Alpha form	phenolic	6:1	310	5	A
X-form	epoxy-urea-formaldehyde	6:1	640	10	A
X-form	epoxy-B.P.A. resin	6:1	630	5	A
Alpha form	B.P.A.-epoxy-urea formaldehyde copolymer	4.5:1	490	60	A
X-form	tall-oil modified epoxy	3:1	350	0	A
X-form	tall-oil modified epoxy	6:1	400	5	A
X-form	tall-oil modified epoxy	10:1	550	5	A
X-form	copolymer of B.P.A. and epichloro-hydrin	14:1	290	25	A
X-form	polyvinyl chloride acetate copolymer	6:1	90	15	A
X-form	RMD-4511	10:1	450	50	A

B.P.A. - bisphenol A
*Alpha converted to the X-form in situ
**Alpha converted to the beta form in situ

EXAMPLES 45–56

As noted earlier in this disclosure, the choice of binder is an important consideration in preparation of the xerographic plate. While positive results are obtained (image produced) with all of the following resins, the image quality varied within a relatively large area. The photoconductive layer is made by milling the phthalocyanine with the resin solution until the desired dispersion is obtained, then applying the mix to a supporting substrate. The phthalocyanine used in all the following runs is Monolite Fast Blue GS. The following table indicates the results:

Resin Binder	Resin to Phthalo-Cyanine Weight Ratio	Charge Accept-ance Volts	Charge Retention Volts — After Exposure	Image Quality
SR-82	25:1	not available		C
Acryloid B-72	10:1	not available		C
Pliolite S-7	50:1	not available		C
VYNS-3	9:1	not available		B
Lucite-46	6:1	not available		B
PS-2	20:1	not available		C
Lucite-42	10:1	450	60	B
Pliolite V-T	14:1	425	85	B
Vinac B-100	7.5:1	435	95	C
Pliolite VTL	10:1	340	100	C
VYHH (vinyl acetate vinyl chloride copolymer)	10:1	375	100	D
Epidene	10:1	460	20	A

EXAMPLES 57–105

A variety of resins are selected and mixed in the heretofore mentioned method to prepare a photoconductive layer for use on a reusable xerographic plate. These resins are investigated in reusability tests as described above; the results are as follows:

RESIN	PHTHALOCYANINE	RESIN: PHTHALOCYANINE WEIGHT RATIO	REUSABILITY RATING*
Araldite 571-K	Monolite Fast Blue GS	17.5/1 35/1	C
Araldite 6040 Phthalic Anhydride	Monolite Fast Blue GS	50/1	C
Araldite 6040 Furoic acid	Monolite Fast Blue GS	33/1	C
Araldite 6040 RMD 4511	Monolite Fast Blue GS	16/1	B
Araldite 6040 RMD 4511	Monolite Fast Blue GS	23/1	C
Araldite-571-K-70 Araldite 6040	Monolite Fast Blue GS	43/1	B
Araldite 6040 VYHH	Monolite Fast Blue GS	22/1	B
Araldite 6040 VYHH	Monolite Fast Blue GS	27/13	B
Araldite 6040 Eponol 55-B-40	Monolite Fast Blue GS	33/1	C
Araldite 6040 Eponol 55-B-40	Monolite Fast Blue GS	20.5/1	C
Araldite 6040 Eponol 55-B-40	Monolite Fast Blue GS	20.2/1	C
DC Silicone R-5061	Monolite Fast Blue GS	20/1	B
DC Silicone R-5061	Monolite Fast Blue GS	10/1	B
Epidene 168/50	Monolite Fast Blue GS	25/1	B
Epidene 168/50	Monolite Fast Blue GS	12.5/1	B
Epidene 168/50	X-form	25/1	B
Epidene 168/50 plus cobalt or manganese driers	Monolite Fast Blue GS	25/1	C
Geon 222	Monolite Fast Blue GS	10/1	C
Parlon	Monolite Fast Blue GS	31/1	C
Pliolite S-5	Monolite Fast Blue GS	10/1	B
Pliolite VT	Monolite Fast Blue GS	10/1–14/1	B
Pliolite VTL	Monolite Fast Blue GS	10/1	B
Pliolite VTLMX	Monolite Fast Blue GS	10/1	B
RMD 4511	Monolite Fast Blue GS	6/1	B
RMD 4511	Monolite Fast Blue GS	8/1	B
RMD 4511	Monolite Fast Blue GS	10/1	B
RMD 4511	X-form	9/1	B
RMD 4511	X-form	10/1	B
RMD 4511	X-form	10/1	B
RMD 4511	X-form	10/1	B
RMD 4511	X-form	20/1	B
RMD 4511	X-form	30/1	B
Vinac B-100	Monolite Fast Blue GS	7.5/1	B

RESIN	PHTHALOCYANINE	RESIN: PHTHALOCYANINE WEIGHT RATIO	REUSABILITY RATING*
Vinyl-epoxy copolymer	Monolite Fast Blue GS	18/1–25/1	C
Tygon TP-107B	Monolite Fast Blue GS	10/1	C
VMCH	Monolite Fast Blue GS	10/1	C
Oxiron 2002	X-form	6/1	B
Epoxy-phenolic	Monolite Fast Blue GS	6/1	A
Epoxy-phenolic	Alpha to X form in situ	6/1	A
Epoxy-phenolic	Alpha to beta in situ	6/1	A
Epoxy-phenolic	X-form	6/1	A
Epoxy-phenolic	X-form	4/1	A
Epoxy-phenolic	Beta form	6/1	A
Phenolic	X-form	6/1	A
Epoxy-urea formal-dehyde resin	X-form	6/1	A
Epoxy-phenolic	Alpha to X-form	12/1	A
Epoxy-phenolic	X-form	12/1	A

*A - good reusability
B - fair reusability
C - poor reusability

EXAMPLES 106–116

Some of the photoconductive layers are adapted more readily for reusability than others, while many of the less reusable plates are improved significantly by overcoating. The overcoating is made from a mixture containing 5 ml. of a solution of 5 grams orange shellac in 50 ml. of ethanol. To this solution is added 0.5 ml. of A-B sensitizer (a dichromate solution) which is sold by the Colonial Processing Supply Company. After the solution is mixed about two drops of a 30 percent aqueous ammonia solution is added. This solution is applied to the plate by drawdown using a Number 14 rod.

The results of various resins are indicated below:

RESIN	PHTHALOCYANINE	RESIN TO PHTHALOCYANINE WEIGHT RATIO	REUSABILITY WITH OR WITHOUT OVERCOATING
Epidene 168/50	X-form	3:1	B
Epidene 168/50	X-form	25:1	B
Araldite 571K	X-form	6:1	A
Epoxy-phenolic	Alpha to beta in situ	6:1	A
Epoxy-phenolic	X-form	6:1	A
Epoxy-phenolic	X-form	4:1	A
Epoxy-phenolic	Beta form	6:1	A
Phenolic	X-form	6:1	A
Epoxy-urea-formaldehyde	X-form	6:1	A
Epoxy-phenolic	Alpha to X-form in situ	12:1	A
Epoxy-phenolic	X-form	12:1	A

A-reusable without overcoating
B-requires overcoating for reusability

EXAMPLES 117–127

A variety of plates are made which are reusable and a comparison is made of the image quality of the first and last images formed. The quality varies, as does the number of images made with various plates.

Results of tests on reusability of both overcoated and unovercoated plates are indicated in the following table:

PHTHALOCYANINE AND RESIN	RESIN TO PHTHALOCYANINE RATIO	NUMBER OF IMAGES MADE	EVALUATION OF FIRST IMAGE	EVALUATION OF LAST IMAGE
Epidene 168/50 X-form	3:1	35	A	A
Epidene 168/50 and X-form	*25:1	7	A	A
X-form and Araldite 571K	6:1	5	A	A
Alpha to beta in situ Epoxy-phenolic	6:1	5	A	A
X-form and Epoxy-phenolic	6:1	5	A	A
X-form and Epoxy-phenolic	4:1	5	A	A
Beta form and Epoxy-phenolic	6:1	5	A	A
X-form and Phenolic	6:1	5	A	A
X-form and epoxy-urea formaldehyde	6:1	5	A	A
Alpha to X-form in situ and Epoxy-phenolic	12:1	5	A	A
X-form and Epoxy Phenolic	12:1	5	A	A

*overcoated plates
A - very good images

EXAMPLE 128

One part of alpha-form metal free phthalocyanine powder is blended with five parts by weight of powdered selenium on an aluminum plate and spread in a uniform layer over the plate surface. This mixture is then heated above 217°C. (the melting point of selenium) so that the molten selenium wets the phthalocyanine particles and the whole plate is then quenched in water to prevent crystal growth and retain the selenium in its amorphous form. The plate is then charged, exposed and developed by conventional xerographic techniques and its response is compared with that of an ordinary amorphous selenium xerographic plate containing no phthalocyanine. A very noticeable increase in red light response and overall photographic sensitivity is observed.

EXAMPLE 129

The procedure of Example 128 is repeated except that instead of using pure selenium, a 99 – 1 percent selenium arsenic alloy powder is blended with the phthalocyanine powder in the same ratio of 1 to 5 parts by weight. This plate produces essentially the same results except for a slightly improved red response over that of the plate produced according to Example 128.

EXAMPLES 130 – 131

A melt of 85 parts of polyvinyl carbazole, 15 parts polypropylene, 5 parts of 2,4,7-trinitrofluorenone and .005 parts of brilliant green dye is well blended and divided into two equal parts. One part is employed to make up a xerographic plate of Example 130 by simply coating it in a thin uniform layer of about 60 micron thickness on aluminum foil and allowing it to cool. To the other portion of the hot melt there is added one part by weight of the alpha form of metal-free phthalocyanine to each 5 parts by weight of the hot melt which is then coated on a similar aluminum. Each of these plates is then allowed to cool and tested according to the procedure of Example 128. While images are produced on both plates, a much increased response in the red end of the visible spectrum and faster overall speed is evidenced by the Example 131 plate.

EXAMPLES 132 – 133

Fifty parts by weight of 2,5-bis(p-aminophenyl), 1,3,4-oxadiazole, 50 parts by weight of an 85/15 copolymer of vinyl chloride and vinyl acetate and 5 parts by weight of 2,4,7-trinitrofluorenone are dissolved in sufficient toluene to make a free-flowing solution which is divided in two halves. The first half is coated on a sheet of aluminum foil and force dried in a warming oven. To the other half of the solution there is added one part of the alpha form of metal-free phthalocyanine to each 6 parts of dissolved solids followed by vigorous agitation to disperse the phthalocyanine particles throughout the solution. The suspension thus formed is then coated on a second sheet of aluminum foil and force dried under the same conditions em-

ployed to dry the plate of Example 130. Both plates are then tested according to the procedure of Example 128 and although they are significantly slower than the plates of Examples 130 and 131, there still seems to be very significantly higher red response and higher overall light sensitivity in the film containing the metal-free phthalocyanine as compared with the one which does not.

EXAMPLE 134

Six parts by weight of the X-form of metal-free phthalocyanine is well dispersed in 5 parts by weight of a very low melting glass enamel frit. This particle mixture is then applied to a uniform thickness over the surface of a stainless steel plate which is then fired under a vacuum to melt the glass and rapidly cool to room temperature. After breaking the vacuum, the plate is tested according to the procedure of Example 128 and found to produce a good quality xerographic image with significant response in the red portion of the visible spectrum.

EXAMPLE 135

One part by weight of X-phthalocyanine is dispersed to 6 parts by weight of melted sucrose. The mixture is coated onto an aluminum plate to a uniform thickness and cooled to room temperature. The plate is xerographically charged and exposed. It retains charge, shows good photoresponse, and can be imaged and developed by standard xerographic techniques. Sensitivity is excellent.

EXAMPLE 136

A melt of boric acid (Baker Analyzed Reagent) is prepared by heating the boric acid in an oven at 240°C. One part by weight of X-phthalocyanine is well dispersed in 6 parts of the boric acid melt. The mixture is coated onto an aluminum plate and cooled to room temperature. The resultant xerographic layer can be charged and imaged but its sensitivity is only about 1/10 that of the sucrose plate of Example 135.

Although various embodiments are directed specifically to the above examples, many of the typical materials mentioned above, if suitable, may be substituted in the examples with similar results. Other materials or additives may be used together with the phthalocyanines and binders of this invention to further enhance, modify, synergize, or in other ways affect the plates of this invention. In addition, the parts, percentages, materials and disclosure of parent application Ser. No. 375,191 are included by reference in the present application. Various modifications will become apparent to those skilled in the art upon a reading of this disclosure; these are intended to be encompassed within the scope of this invention.

What is claimed is:

1. An electrophotographic material comprising phthalocyanine pigment particles dispersed in a binder material and a spectral sensitizing agent for said phthalocyanine pigment, said phthalocyanine particles being present in said binder in an amount up to about 50 percent by weight and said binder having a resistivity greater than about 10^{10} ohm/cm.

2. An electrophotographic plate which comprises a photoconductive layer substantially uniformly coated to a thickness of up to about 80 microns on a substrate material, said photoconductive layer comprising phthalocyanine pigment particles dispersed in a binder material, said phthalocyanine being selected from the group consisting of beta-form phthalocyanine and X-form phthalocyanine and mixtures thereof, and said binder material having a resistivity greater than about 10^{10} ohm/cm.

3. The plate of claim **2** wherein said phthalocyanine pigment particles are present in said binder material in an amount up to about 50 percent weight.

4. The plate of claim **2** wherein said phthalocyanine pigment particles are metal-free.

5. The plate of claim **2** wherein said substrate material comprises paper.

6. The plate of claim **2** wherein said substrate material is substantially conductive.

7. The plate of claim **2** further comprising a substantially dielectric overcoating material overlying said photoconductive layer.

8. The plate of claim **2** wherein said binder material is substantially photoconductive.

9. The plate of claim **8** wherein said binder comprises polyvinylcarbazole.

10. The plate of claim **8** wherein said binder comprises selenium.

11. An electrophotographic process wherein the plate of claim **2** is electrostatically charged and exposed to a pattern of activating electromagnetic radiation.

12. An electrophotographic process wherein the plate of claim **2** is electrically charged, exposed to an image pattern to be reproduced and developed with electroscopic marking particles.

13. An electrophotographic process which comprises passing the plate of claim **2** at least twice through a cycle comprising charging and exposing said plate to a pattern of activating electromagnetic radiation and developing.

14. A process for forming an image which comprises exposing in imagewise configuration a photoconductive layer positioned on a paper substrate material, said layer comprising phthalocyanine pigment dispersed in a binder material to form a latent electrostatic image, and developing said image.

15. A process for forming an image which comprises exposing in imagewise configuration a photoconductive layer comprising phthalocyanine pigment dispersed in a binder material to form a latent electrostatic image, and developing said image.

16. The process of claim **15** wherein said photoconductive layer is overcoated with an insulating composition.

17. The process of claim **15** wherein at least one image is formed at the surface of said photoconductive layer.

18. A process for forming a latent electrostatic charge pattern which comprises electrostatically charging a photoconductive layer comprising phthalocyanine pigment dispersed in a binder material, and exposing said layer to a pattern of activating electromagnetic radiation.

19. A process for forming a latent electrostatic charge pattern on an electrophotographic plate, said plate comprising a photoconductive layer comprising phthalocyanine pigment dispersed in a binder material, in electrical contact with a supporting substrate, which comprises electrostatically charging the photoconduc-

tive layer of said plate and exposing said layer to a pattern of activating electromagnetic radiation.

20. An electrophotographic process which comprises electrically charging an electrophotographic plate, said plate comprising phthalocyanine pigment dispersed in a binder material, exposing said plate to an image pattern to be reproduced, and developing said image.

21. An electrophotographic process which comprises passing an electrophotographic plate at least twice through a cycle comprising charging and exposing said plate to a pattern of activating electromagnetic radiation and developing with electrically attractable marking material.

22. A process for forming a latent image which comprises exposing in imagewise configuration a photoconductive composition comprising a matrix of a substantially non-photoconductive organic polymer containing a substantially uniform dispersion of particles of a photoconductive pigment selected from the group consisting of phthalocyanine and metal derivatives of phthalocyanine.

23. A process for forming a latent electrostatic charge pattern which comprises electrostatically charging and exposing a photoconductive composition comprising a matrix of a substantially non-photoconductive organic polymer containing a substantially uniform dispersion of particles of a photoconductive pigment selected from the group consisting of phthalocyanine and metal derivatives of phthalocyanine.

24. A process for forming a latent electrostatic charge pattern on an electrophotographic plate, said plate comprising a supporting substrate in electrical contact with a photoconductive composition comprising a matrix of a substantially non-photoconductive organic polymer containing a substantially uniform dispersion of particles of photoconductive pigment selected from the group consisting of phthalocyanine and metal derivatives of phthalocyanine, which comprises electrostatically charging and exposing said photoconductive composition.

25. An electrophotographic process which comprises electrically charging an electrophotographic plate, said plate comprising a photoconductive composition comprising a matrix of a substantially non-photoconductive organic polymer containing a substantially uniform dispersion of particles of a photoconductive pigment selected from the group consisting of phthalocyanine and metal derivatives of phthalocyanine, exposing said plate to an image pattern to be reproduced, and developing with electrostatically attractable marking material.

26. A process for forming a latent image which comprises exposing in imagewise configuration a photoconductive layer comprising phthalocyanine pigment particles dispersed in a binder material, said phthalocyanine being a primary photosensitive material in said layer and being present in said photoconductive layer in an amount up to about 50 percent by weight.

27. A process for forming a latent electrostatic charge pattern which comprises electrostatically charging a photoconductive layer and exposing said layer to a pattern of activating electromagnetic radiation, said photoconductive layer comprising phthalocyanine pigment particles dispersed in a binder, said phthalocyanine being a primary photosensitive material in said layer and being present in said photoconductive layer in an amount up to about 50 percent by weight.

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