

RESERVE COPY

PATENT SPECIFICATION

1,116,553



DRAWINGS ATTACHED

1,116,553

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Int. Cl.:—G 03 g 1/04

COMPLETE SPECIFICATION

Electrophotographic Element

We, RANK XEROX LIMITED, of Mortimer House, 37—41 Mortimer Street, London, W.1., a British Company do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

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 British specification No. 672,767 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 specification, 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 prior art as being useful in similar electrophotographic processes. Some of these materials are vitreous selenium, polymers such as polyvinylcarbazole, and resin suspensions of inorganic photoconductive pigments such as, zinc oxide and cadmium sulfide. While most of these materials have evidenced some com-

mercial 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 wavelengths shorter than about 5,800 A.U. In addition, xerographic plates made with selenium are very expensive to manufacture since this material must be applied to the supporting substrate by vacuum evaporation under highly controlled conditions. Also, vitreous selenium layers are only meta-stable because they are readily re-crystallized into inoperative crystallized forms at temperatures only slightly in excess of those prevailing in conventional xerographic copying machines. For these reasons such plates may have a comparatively limited life upon repeated use.

Other known xerographic plates such as the aromatic binder plates have relatively low sensitivity to light, have most of this sensitivity in the ultra-violet range, and even the further sensitized plates do not have sensitivities to levels fully satisfactory for use in conventional electrophotographic copying devices. The aromatic polymer plates are somewhat more sensitive than the binder plate but still leave much to be desired for commercial purposes. The choice of materials available for use in aromatic polymer plates are 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.

Aromatic binder plates containing zinc oxide pigments, while comparatively inexpensive, differ in sensitivity to vitreous selenium plates and are generally considered to be substantially unrecusable. Also, as above noted, their

sions 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.

When it is desired to coat the phthalocyanine-resin 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. Phthalocyanines are known to exist in several interconvertible crystal forms. These forms are described in detail in a book entitled "Phthalocyanine Compounds" by F. H. Moser and A. L. Thomas, published by the Reinhold Publishing Company, 1963 edition. Any suitable phthalocyanine discussed in this book may be used in the present invention. Phthalocyanines 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, 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.

45 It has been found in the present invention that suspensions of phthalocyanine pigments in resin binders are not only capable of sustaining the very high fields required in commercial xerography, but are also simultaneously highly
50 photoconductive. Since a wide variety of resin binders may be used in the present invention, for example, varying from soft thermoplastics to hard cross linked enamels, and since percentages of phthalocyanine required in these
55 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
60 used may therefore be varied over a wide range by selection of the appropriate resins to suit the specific requirements of each particular situation. In this regard, these photoconductive layers are substantially different
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cyanine, copper phthalocyanine sulfonate, copper polychlorophthalocyanine, deuterio-phthalocyanine, 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, alkylamino-phthalocyanine, alkylmercaptophthalocyanine, aralkylaminophthalocyanine, aryloxyphthalocyanine, arylmercaptophthalocyanine, copper phthalocyanine piperidine, cycloalkylamino-dialkylaminophthalocyanine, dicycloalkylaminophthalocyanine, hexadecahydrophthalocyanine, imidomethylphthalocyanine, 1,2 naphthalocyanine, 2,3 naphthalocyanine, octa-azaphthalocyanine, sulfur phthalocyanine, tetraazaphthalocyanine, tetra - 4 - acetylaminophthalocyanine, tetra - 4 - aminobenzoylphthalocyanine, tetra - 4 - aminophthalocyanine, tetrachloromethylphthalocyanine, tetradiazaphthalocyanine, tetra - 4,4-dimethylocta - azaphthalocyanine, tetra - 4,5-diphenylenedioxide phthalocyanine, tetra-4,5 - diphenylocta - azaphthalocyanine, tetra-(6 - methyl - benzothiazoyl) phthalocyanine, tetra - p - methylphenylaminophthalocyanine, tetramethylphthalocyanine, tetra - naphthotriazolylphthalocyanine, tetra - 4 - naphthylphthalocyanine, tetra - 4 - nitrophthalocyanine, tetra - peri - naphthylene - 4,5-octa - azaphthalocyanine, tetra - 2,3 - phenyleneoxide phthalocyanine, tetra - 4 - phenylocta - azaphthalocyanine, tetraphenylphthalocyanine, tetraphenylphthalocyanine tetracarboxylic acid, tetraphenylphthalocyanine tetrabarium carboxylate, tetraphenylphthalocyanine tetra - calcium carboxylate, tetrapyriddyphthalocyanine, tetra - 4 - trifluoro - methylmercaptophthalocyanine, tetra - 4 - trifluoromethylphthalocyanine, 4,5 - thionaphthene - octaazaphthalocyanine, platinum phthalocyanine, potassium phthalocyanine, rhodium phthalocyanine, samarium phthalocyanine, silver phthalocyanine, silicon, phthalocyanine, sodium phthalocyanine, sulfonated phthalocyanine, thorium phthalocyanine, thulium phthalocyanine, tin chlorophthalophthalocyanine, tin phthalocyanine, titanium phthalocyanine, uranium phthalocyanine, vanadium phthalocyanine, ytterbium phthalocyanine, zinc

chlorophthalocyanine, zinc phthalocyanine. Together with, or in lieu of, the above phthalocyanines, any suitable mixture, dimer, trimer, oligomer, polymer, copolymer or mixtures thereof of phthalocyanines may be used.

Any suitable organic binder or resin may be used in combination with the phthalocyanine to prepare the photoconductive layer of this invention. In order to be useful the resin used in the present invention is preferably more resistive than 10^{11} and preferably more than 10^{12} ohm/cm. under the conditions of xerographic use. Typical resins are thermoplastics such as polyvinylchloride, polyvinylacetates, polystyrene, polystyrenepolybutadiene copolymers, polymethacrylates, polyacrylics, polystyrene, silicone resins, chlorinated rubber, and mixtures and copolymers thereof where applicable. Thermal setting resins such as epoxy resins including halogenated epoxy and phenoxy resins, phenolics, epoxy-phenolic copolymers, epoxy urea formaldehyde copolymers, epoxy melamine formaldehyde copolymers and mixtures thereof where applicable. Other typical resins are epoxy esters, vinyl epoxy resins, tall-oil modified epoxys, and mixtures thereof where applicable. In addition to the above noted binder materials, any other suitable resin may be used if desired.

The phthalocyanine pigments may be incorporated in the dissolved or melted binder resin by any suitable means such as strong sheer 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. The range of pigment-resin ratio which may be used, on a phthalocyanine pigment-dried resin weight basis, extends from 1/1 to 1/20. Best results are obtained at, and therefore the preferred range is, from 1/4 to 1/20. Optimum results were obtained when ratios from 1/6 to 1/12 were used. 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-resin ratio drops below 2/1.

The ability in the present invention to use lower pigment to resin 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, for example, one may choose resins having the desired softening range, smooth-

ness, hardness, toughness, solvent resistance, or solubility, and water repellency with assurance that the pigment will not affect these properties to any considerable extent.

5 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 spray, flow coating, knife-coating, electro-coating, 10 Mayer bar draw-down, dip coating and reverse roll coating. 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 15 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 20 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 25 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 30 appliance resin enamels.

The thickness of the phthalocyanine films may be varied for example from 1 to 100 35 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 40 range. Coatings, on the other hand, are preferably in the 5 to 30 micron range, 15 microns being in the middle of the broad optimal range thicknesses. For certain compositions and purposes it is desirable to provide an over- 45 coating; this should usually not exceed the thickness of the photoconductive coating, and preferably not above 1/4 of the latter. Any suitable overcoating material may be used such as bichromated shellac. A series of detailed 50 examples indicating our preferred procedure of making the plate by mixing, milling, and coating is presented below.

While any suitable phthalocyanine or mixtures of phthalocyanines may be used in the present invention, it has been found that for 55 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 60 phthalocyanine such as alpha, beta, and what is hereinafter referred to as the "X" form of phthalocyanine. The exact physical structure of the "X" form phthalocyanine is not presently understood, however it is recognised 65 as being different from the alpha, beta and gamma forms by its distinct x-ray diffraction

pattern and its infrared spectrum which is indicated in accompanying drawings 1 to 4. In the drawings:

Fig. 1 shows x-ray patterns reported in the literature for each of the known polymorphs and for X-form in vertical alignment 70 for easy comparison.

Fig. 2 shows infrared patterns reported in the literature for each of the known polymorphs and for X-form. 75

Fig. 3 shows x-ray patterns for alpha, beta and X-form polymorph for samples prepared in the laboratory.

Fig. 4 shows infrared patterns for alpha, beta and X-form polymorph for samples prepared in the laboratory. 80

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, 85 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- 90 electric Properties of the Modifications 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 95 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 22.3 100 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, 105 16.7, 17.3 and 22.3.

Fig. 2 shows a comparison between an experimentally obtained infrared spectra for X-form metal-free phthalocyanine and infrared 110 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 115 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 120 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 125 forms. The variation in peak intensity and location for the different polymorphic forms is especially noticeable in the 700—800 cm^{-1} and 1250—1350 cm^{-1} regions.

Fig. 3 shows a set of curves comparing 130

ndi- the			alpha, beta and X-forms of metal-free phthalocyanine arranged in a manner similar to that of Fig. 1. The samples of each form of phthalocyanine tested by x-ray diffraction	65
in oly- nent	70	5	was prepared in the laboratory and analyzed on the same equipment by the same operator to insure consistency. The samples used to produce the curve for alpha form was commercial Monolite Fast Blue GS, a mixture of alpha and beta metal-free phthalocyanine available from the Arnold Hoffman Co., a division of ICI, Ltd. This pigment was entirely converted to alpha form before testing by solvent extraction with dichlorobenzene washing with acetone and precipitation from sulfuric acid in ice water. The beta form sample which produced the curve shown in Fig. 3 was prepared by suspending commercial Monolite Fast Blue GS in triethylenetetramine at a concentration of 1 part pigment to 5 parts triethylenetetramine by weight for four days at about 23°C. The pigment was then washed with methanol and dried.	
in oly-	75	10	The X-form phthalocyanine which produced the curve shown at Figs. 1 and 3 was prepared as follows. Commercial Monolite Fast Blue GS was solvent extracted with dichlorobenzene, then washed with acetone and dried. The pigment was then dissolved in sulfuric acid and precipitated in ice water. The precipitate was washed with methanol and dried. The pigment was then neat milled in a ball mill for 7 days, washed with dimethyl formamide and then with methanol.	
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pha, re-	80			
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as 2.3	90			
ly- 0.1 he X-		30		
1,	95			
x- X- ed ee e. a- re ty or	100	35		
re le e a is is a r e a d s i	105	40		
		45		
	110			
		50		
	115			
		55		
	120			
		60		
	125			
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prepared samples of alpha and beta phthalocyanine agree with those in the literature as shown in Fig. 2. The spectra for X-form phthalocyanine differs markedly from those for alpha, and beta forms.

In characterizing the alpha, β and X-forms, the position of four C—H deformation bands may be considered. For the alpha form these exist at 708, 724, 728 and 733 cm^{-1} . In the beta form they are shifted to the higher frequencies of 715, 725, 732 and 745. The "X"-form had the same C—H deformation bands as the beta, but in this spectra, differences are shown as a change in the intensity ratio for the 765 and 755 cm^{-1} bands. For the beta, the intensities are nearly equal, but with the "X"-form, the intensity of the 765 cm^{-1} is about twice that of the 755 cm^{-1} band.

Other band changes, such as those between 1250 and 1350 cm^{-1} can be used to characterize the three forms. The relative ratios for the four bands are quite different for the three forms, as can be seen in Fig. 3.

Specification 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, 55.4 g. of a blue powder whose x-ray pattern matched that of the known published pattern for alpha metal-free phthalocyanine is obtained.

Preparation of Beta Metal-Free Phthalocyanine.

A 10 g. supply of commercial Monolite Fast Blue GS is placed in a Vycor dish (VYCOR is a Registered Trade Mark) 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 1—1/2 hours to avoid scattering of sample, and finally maintained at 350—430°C. during the next four 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.

5 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 one per cent hydrochloric acid at 70—80°C. for one 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 the accompanying drawings. 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 (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 mill (NUJOL is a Registered Trade Mark) and subsequently examined under a standard infrared spectrophotometer (Perkin-Elmer Infracord Model No. 137) (INFRACORD is a Registered Trade Mark). Figure 2 shows the infrared spectra of these alpha, beta 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 lipidene) 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 Cyanamide 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:

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his		a. methanolysis of dilithium phthalocyanine	Pliolite S—7 — is a polystyrene-butadiene copolymer made by the B. F. Goodrich Company (PLIOLITE is a Registered Trade Mark);	65
ha	65	b. acid hydrolysis of dilithium phthalocyanine, with optional reprecipitation from sulphuric acid.	Araldite 571—K and 6040 are epoxy resins made by the Ciba Chemical Company (ARALDITE is a Registered Trade Mark);	65
ee			Eponol 55—B—40 — is a modified epoxy resin made by the Shell Chemical Company;	70
nd			DC Silicone R—5061 — is a silicon resin made by the Dow Corning Company;	75
nt	5	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.	Geon 222—is a vinyl acetate-vinyl chloride copolymer made by the Goodyear Chemical Company (GEON is a Registered Trade Mark);	75
it-	70	3. Gamma metal-free phthalocyanine was prepared from calcium phthalocyanine by acid hydrolysis, according to <i>Phthalocyanine Compounds</i> , by Frank H. Moser and Arthur C. Thomas, 1963 edition, published by Reinhold Publishing Corp.	RMD 4511—is a styrene acrylonitrile copolymer made by the Union Carbide Corporation;	80
us		4. "X" form metal-free phthalocyanine was prepared from alpha metal-free phthalocyanine by extended ball milling in salt particles followed by desalting.	Parlon—is a chlorinated rubber made by the Du Pont Company (PARLON is a Registered Trade Mark);	80
IO	10		Pliolite S—5, VT, °VTL, VTLNX—are all vinyl toluene polymers made by the Goodyear Chemical Company;	85
to			Vinac B—100 — is a vinyl acetate resin made by Air Reduction Company (VINAC is a Registered Trade Mark);	90
m	75		Tygon TP—107—B — is an unpigmented metal primer made of a thermoplastic resin made and sold by U.S. Stonewear Company;	95
or			VMCH—is a maleic acid modified acetate-vinyl chloride copolymer made by the Union Carbide Corporation;	100
es	80		Synthtazinc 200—is a thermosetting resin made by the Interchemical Corporation;	100
ed			DER 542—is a brominated epoxy resin made by the Dow Chemical Corporation.	105
to	85			110
ch		B. <i>Metal Phthalocyanines.</i>		115
m		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;		120
rs		Chlorinated Copper phthalocyanine		125
ed		Beta Copper phthalocyanine		
in		Lead phthalocyanine		
ed		Zinc phthalocyanine		
m		It was noticed that the performance of these material in part was a function of the binder resin used, for example copper phthalocyanine and chlorinated copper phthalocyanine which were comparatively inferior in a vinyl resin (VYNS—3) gave an acceptable image in a silicon binder (SR—82).		
n-		In the disclosure various tradenames will be used to define specific resins and phthalocyanines. The following is a list of components identified in the ensuing disclosure identifying the basic chemical structure of each:		
g.		RESINS:		
e-		SR Oxiron 2002—is an epoxidized polyolefin made by the FMC Corporation;		
ic		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;		
es		SR—82 — is a silicone resin made by the General Electric Company;		
g-		Acryloid B—72 — is a polyacrylate made by the Rohm & Haas Company;		
iS		Lucite 44 and 46 are polymethacrylates made by the DuPont Company;		
ti-		PS—2 — is a polystyrene resin made by the Pennsylvania Industrial Chemical Company;		
IO		Nitrocellulose made by the Hercules Powder Company;		
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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 20% 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, dibenzyl ether, 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 in Xerox Number 1 Camera and using a Xerox Flat Plate apparatus. The developer used was a commercially available xerographic de-

veloper. 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 cyclically 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. 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 preceding 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 were charged, exposed and developed in the conventional xerographic method and produced images ranging in quality. These images will be designated in comparative terms in the ensuing examples. Very good images will be designated by the symbol "A", good images will be 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 draw-down 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 testing 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

were 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.

100. The milled mixture may be stored prior to deposition on the supporting substrate.

Aluminum foils are used as the supporting substrate and the finished 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 pre-charge processing which could be merely heat curing or may involve a sublimation-doping step. In instances where undiluted liquid addition doping is performed the dopant liquid is added to the coating mixture before coating on the aluminum foil.

General Preparation of Xerographic Plates Used in the Following Examples.

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

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 Retention 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

5 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

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EXAMPLES 17—28.

The phthalocyanines used in this example 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:

Phthalocyanine	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
Aluminium	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:

Phthalocyanines	Resin	Resin to Phthalocyanine Weight Ratio	Charge Acceptance 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
*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 epichlorohydrin	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.

- 5 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 the below 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 below runs is Monolite Fast Blue GS. The following table indicates the results:

Resin Binder	Resin to Phthalocyanine Weight Ratio	Charge Acceptance 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 (Lucite is a Registered Trade Mark)	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	425	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:

5

Resin	Phthalocyanine	Resin: Phthalocyanine Weight Ratio	Reusability Rating*
Araldite 571—K	Monolite Fast Blue GS	17.5/1 35/1	C 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 RMD4511	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	27/1	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
Gcon 222	Monolite Fast Blue GS	10/1	C

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Resin	Phthalocyanine	Resin: Phthalocyanine Weight Ratio	Reusability Rating*
Parlon	Monolite Fast Blue GS	13/1	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
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

Resin	Phthalocyanine	Resin: Phthalocyanine Weight Ratio	Reusability Rating*
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-urca formaldehyde 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

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EXAMPLES 106—116.

5 Some of the photoconductive layers were 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 di-

chromate solution) which is sold by the Colonial Processing Supply Company. After the solution is mixed about two drops of a 30% 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 below 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-urca 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

Attention is drawn to our copending application No. 2593/68 Serial No. 1116554 which relates to the X-form of metal-free phthalocyanines.

15 WHAT WE CLAIM IS:—

1. An electrophotographic plate comprising a photoconductive layer containing a phthalocyanine and a binder material wherein the ratio of phthalocyanine to binder material on a dry weight basis is from 1:1 to 1:20.

20 2. The plate of claim 1 wherein said binder material is an organic resin binder.

3. The plate of claim 1 or 2 wherein said phthalocyanine is unsubstituted.

4. The plate of claim 1 or 2 wherein said phthalocyanine is an unsubstituted metal-free phthalocyanine.

5. The plate of claim 1 or 2 wherein said phthalocyanine is in the X-crystalline form of unsubstituted metal-free phthalocyanine.

6. The plate of claim 1 or 2 wherein said phthalocyanine is in the alpha crystalline form of unsubstituted metal-free phthalocyanine.

7. The plate of claim 1 or 2 wherein said phthalocyanine is in the beta crystalline form of unsubstituted metal-free phthalocyanine.

8. The plate of any preceding claim wherein said photoconductive layer is a self-supporting layer.

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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 below 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

Attention is drawn to our copending application No. 2593/68 Serial No. 1116554 which relates to the X-form of metal-free phthalocyanines.

15 WHAT WE CLAIM IS:—

1. An electrophotographic plate comprising a photoconductive layer containing a phthalocyanine and a binder material wherein the ratio of phthalocyanine to binder material on a dry weight basis is from 1:1 to 1:20.

20 2. The plate of claim 1 wherein said binder material is an organic resin binder.

3. The plate of claim 1 or 2 wherein said phthalocyanine is unsubstituted.

4. The plate of claim 1 or 2 wherein said phthalocyanine is an unsubstituted metal-free phthalocyanine.

5. The plate of claim 1 or 2 wherein said phthalocyanine is in the X-crystalline form of unsubstituted metal-free phthalocyanine.

6. The plate of claim 1 or 2 wherein said phthalocyanine is in the alpha crystalline form of unsubstituted metal-free phthalocyanine.

7. The plate of claim 1 or 2 wherein said phthalocyanine is in the beta crystalline form of unsubstituted metal-free phthalocyanine.

8. The plate of any preceding claim wherein said photoconductive layer is a self-supporting layer.

9. The process of said claim 1 wherein said photoconductive layer has a thickness of 5 to 75 microns.

10. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member.

11. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible.

12. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

13. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

14. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

15. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

16. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

17. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

18. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

19. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

20. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

21. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

22. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

23. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

24. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

25. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

26. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

27. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

28. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

29. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

30. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

31. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

32. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

33. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

34. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

35. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

36. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

37. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

38. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

39. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

40. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

41. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

42. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

43. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

44. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

45. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

46. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

47. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

48. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

49. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

50. The plate of claim 1 wherein said photoconductive layer is supported on a supporting member which is flexible and has a thickness greater than 10 microns.

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9. The plate of claim 8 wherein the thick-
ness of said photoconductive layer is from
15 to 75 microns.
10. The plate of any of claims 1 to 7
5 wherein said photoconductive layer is posi-
tioned on a supporting substrate.
11. The plate of claim 10 wherein said
supporting substrate is electrically conductive.
12. The plate of claim 9 wherein the thick-
10 ness of said photoconductive layer is from
5 to 30 microns.
13. The plate of any preceding claim wherein
said photoconductive layer is overcoated.
14. The plate of claim 10 wherein said
15 photoconductive layer is provided with an
overcoating the thickness of which is not
greater than one quarter of the thickness of
the photoconductive layer.
15. The plate of any preceding claim wherein
20 said binder is a substantially insulating resin
which is film forming when mixed with a com-
position comprising a phthalocyanine.
16. The plate of any preceding claim wherein
said binder is a resin selected from the group
25 consisting of polystyrene, silicones, acrylic
esters, methacrylate esters, polyvinyl aliphatics,
epoxys, phenolics, acrylonitriles, mixtures and
copolymers thereof.
17. The plate of any preceding claims
30 wherein the electrical resistivity of said binder
is more than 10^{10} ohm/cm, preferably more
than 10^{12} ohm/cm.
18. The plate of any preceding claim
wherein said ratio is from 1:4 to 1:20.
19. The plate of claim 17 wherein said ratio
35 is from 1:6 to 1:12.
20. A method for the production of a
photoconductive layer of an electrophoto-
graphic plate which comprises mixing a
40 phthalocyanine and an organic resin in a
liquid medium, and the ratio of phthalocyanine
to binder material on a dry weight basis
being from 1:1 to 1:20, and forming a layer
with the mixture thereby produced.
21. The method of claim 20 wherein said
45 liquid medium is a solvent for said resin.
22. The method of claim 20 wherein said
photoconductive layer is deposited on a sup-
porting substrate to form thereby an electro-
50 photographic plate.
23. A method for the production of an
electrophotographic plate which comprises
mixing in a liquid medium a phthalocyanine
and a binder resin, the ratio of phthalocyanine
to binder on a dry weight basis being from 1:1
55 to 1:20, depositing said liquid mix on a
conductive supporting substrate, allowing said
liquid portion of said mix to evaporate there-
from, and forming thereby a substantially solid
photoconductive layer in electrical contact with
60 said substrate.
24. The method of claim 23 wherein said
photoconductive layer is overcoated.
25. A process for forming a latent electro-
static charge pattern on a photoconductive
65 layer comprising a phthalocyanine and an
organic binder, the ratio of phthalocyanine to
binder on a dry weight basis being from 1:1
to 1:20, which comprises electrostatically
charging said layer and exposing said layer
70 to a pattern of activating electromagnetic radi-
ation.
26. A process for forming a latent electro-
static charge pattern on an electrophotographic
plate comprising a photoconductive layer of
75 phthalocyanine and a binder in electrical con-
tact with a supporting substrate, the ratio of
phthalocyanine to binder on a dry weight
basis being from 1:1 to 1:20, which com-
prises electrostatically charging the photo-
80 conductive layer of said plate and exposing
said layer to a pattern of activating electro-
magnetic radiation.
27. An electrophotographic process wherein
the plate of claim 1 is electrically charged;
85 exposed to an image pattern to be reproduced
and developed with electrically attractable
marking particles.
28. An electrophotographic process wherein
the plate of claim 1 is passed at least twice
90 through a cycle comprising charging means,
image exposure means, and image developing
means.
29. Electrophotographic plates as claimed in
claim 1 substantially as herein described. 95

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