

[54] XEROGRAPHIC IMAGING MEMBER
HAVING PHOTOCONDUCTIVE MATERIAL
IN INTER-LOCKING CONTINUOUS PATHS

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[21] Appl. No.: 75,390

Related U.S. Application Data

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1967, abandoned.

[52] U.S. Cl. 96/1.8, 96/1 R, 96/1.5,
117/34, 117/201, 252/501

[51] Int. Cl. G03g 5/04

[58] Field of Search 96/1.5, 1.8; 252/501

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3,121,006 2/1964 Middleton et al. 96/1.5 X
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[57] **ABSTRACT**

A xerographic photoreceptor layer which comprises photoconductive particles dispersed in an insulating resin matrix, the photoconductive particles are present in an amount from about 1 to 25 percent by volume of the layer, and are dispersed in a controlled manner to form a plurality of continuous paths through the thickness of said layer. Methods of making and imaging the photoreceptor layer are also disclosed.

18 Claims, 13 Drawing Figures

SENSITIVITY DEPENDENCE Vs. % CdSSe IN BINDER LAYER

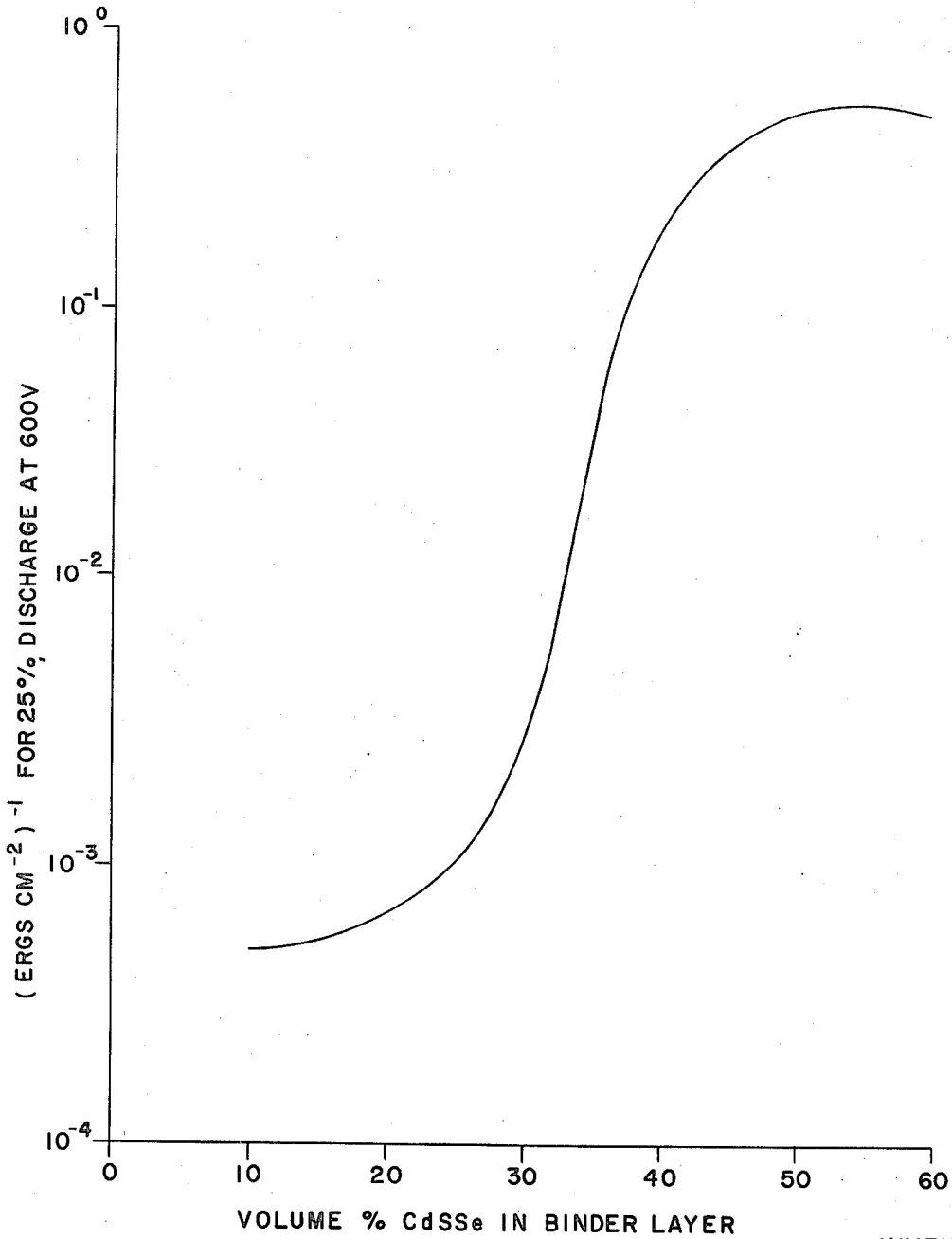
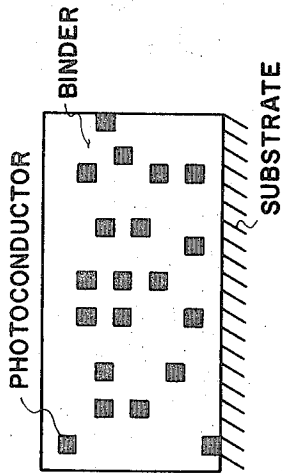


FIG. 1

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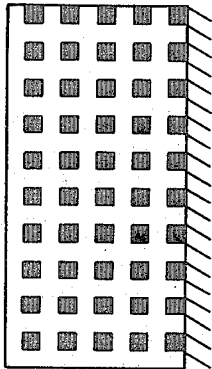
ATTORNEY



10% VOLUME

PHOTOCONDUCTOR CONCENTRATION

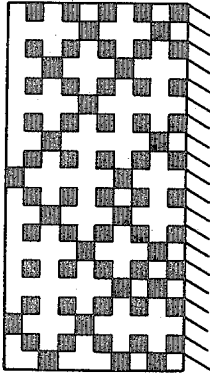
FIG. 2A



25% VOLUME

PHOTOCONDUCTOR CONCENTRATION

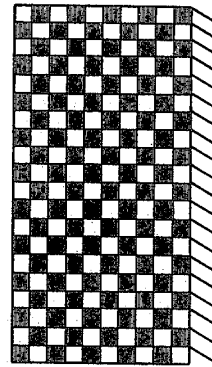
FIG. 2B



30% VOLUME

PHOTOCONDUCTOR CONCENTRATION

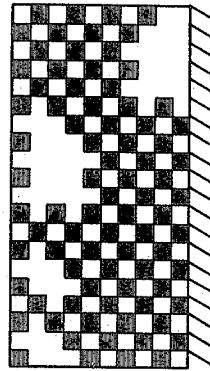
FIG. 2C



50% VOLUME

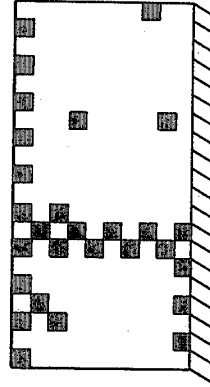
PHOTOCONDUCTOR CONCENTRATION

FIG. 2D



10% OF PHOTOCONDUCTOR
VOLUME REPLACED BY LARGE
RESIN PARTICLES

FIG. 3A



40% OF PHOTOCONDUCTOR
VOLUME REPLACED BY LARGE
RESIN PARTICLES

FIG. 3B

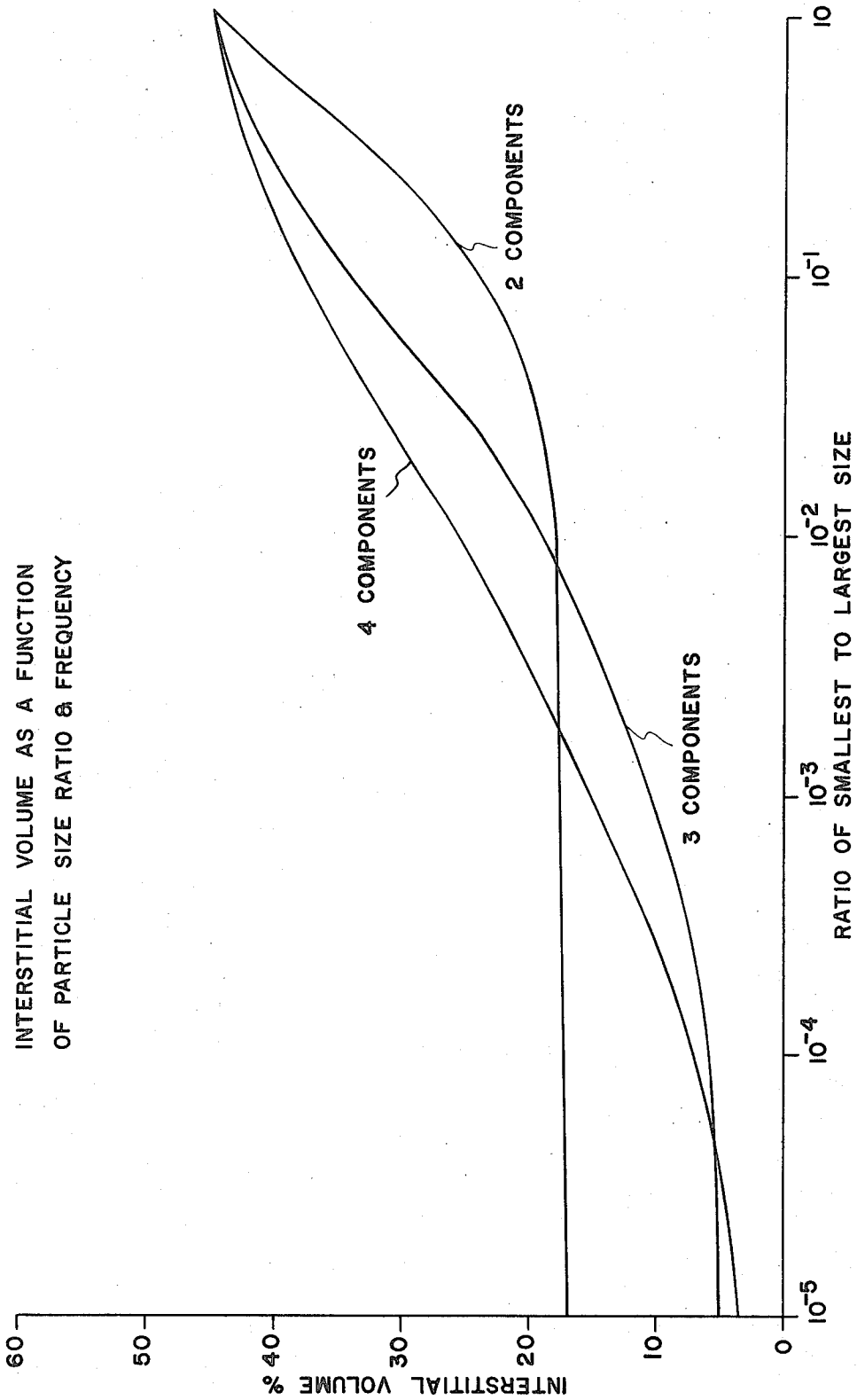


FIG. 4

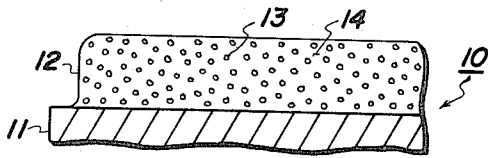


FIG. 5A

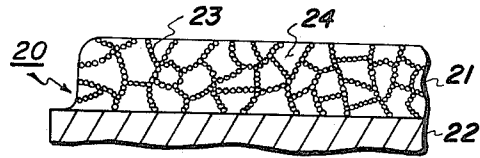


FIG. 6A

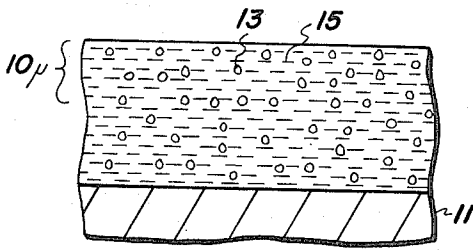


FIG. 5B

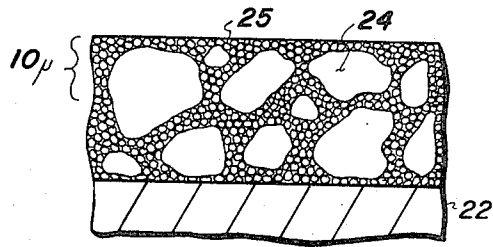


FIG. 6B

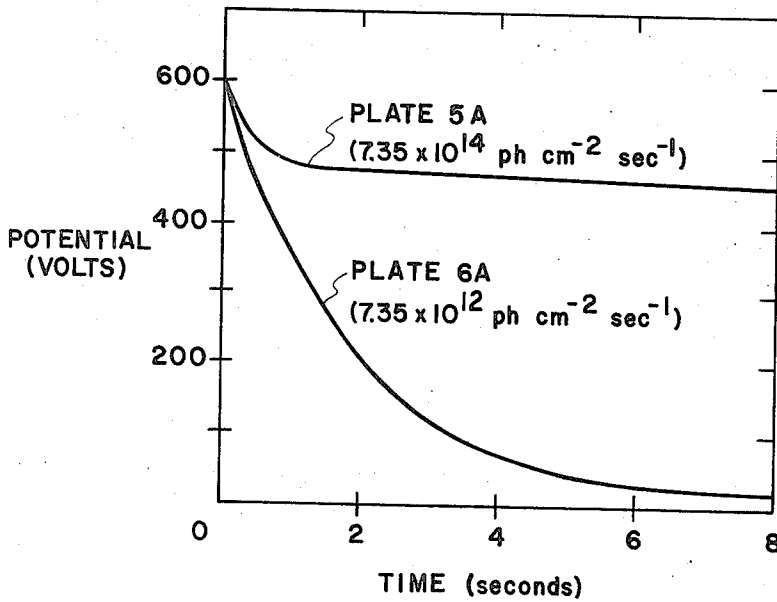


FIG. 7

XEROGRAPHIC IMAGING MEMBER HAVING PHOTOCONDUCTIVE MATERIAL IN INTER-LOCKING CONTINUOUS PATHS

RELATED APPLICATIONS

This application is a continuation-in-part of applicant's copending application, Ser. No. 627,664, filed Apr. 3, 1967 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to xerography and more specifically to a novel photosensitive member and a method of preparing and using such a member.

The art of xerography involves the use of a photosensitive element or plate containing a photoconductive insulating layer which is first uniformly electrostatically charged in order to sensitize its surface. The plate is then exposed to an image of activating electromagnetic radiation such as light, x-ray, or the like which selectively dissipates the charge in the exposed areas of the photoconductive insulator while leaving behind a latent electrostatic image in the non-exposed areas. This latent electrostatic image may then be developed and made visible by depositing a finely-divided, electroscopic marking particle on the surface of the photoconductive layer. This concept was originally disclosed by Carlson in U.S. Pat. No. 2,297,691, and is further amplified and described by many related patents in the field.

One type of photoconductive layer used in xerography is illustrated by U.S. Pat. No. 3,121,006 to Middleton and Reynolds which describes a number of binder layers comprising finely-divided particles of a photoconductive inorganic compound dispersed in an organic electrically insulating resin binder. In its present commercial form, the binder layer contains particles of zinc oxide uniformly dispersed in a resin binder and is coated on a paper backing.

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

It has been found that the employment of a high volume concentration of photoconductor in a xerographic binder layer places stringent requirements on the photoconductor material in terms of dark conductivity and accentuates fatigue effects which result from trapping, long recombination times, and field ionizable state carrier concentrations. In addition, the utilization of low volume binder resin concentrations result in poor mechanical properties in terms of cohesion, adhesion, flexibility, toughness, and/or a porous film which can result in humidity sensitivity and undesirable fatigue effects. At the same time, surface porosity tends to negate residual toner removal and, therefore, the capability of repeatedly cycling the photoreceptor in the xerographic imaging mode.

The optimum volume concentration ratio of photoconductor to resin in these systems is therefore a compromise between photosensitivity and residual level on the one hand, and the mechanical properties and fatigue effects on the other. The actual optimum volume ratio for any specific system is dependent, in general, upon the particle size and density of the photoconductor, and the density and rheological properties of the resin solution in relation to the photoconductor.

It has now been discovered that the optimum volume concentration of a photoconductor in the resin binder systems, such as those illustrated above, can be reduced significantly without sacrificing photosensitivity, if the bulk geometry can be controlled to insure substantial particle-to-particle contact of the photoconductor particles throughout the thickness of the binder layer. Such a reduction in photoconductor concentration should result in enhanced mechanical and surface properties, as well as improved control of the electrical characteristics of the binder layer.

OBJECTS OF THE INVENTION

It is therefore an object of this invention to provide a novel photoconductive binder layer.

It is another object of this invention to provide a method of imaging a photoconductive binder layer.

It is a further object of this invention to provide a novel binder layer having an extremely high binder to photoconductor volume ratio.

It is another object of this invention to provide a method of making a binder layer.

It is yet another object of the instant invention to provide a system utilizing a novel xerographic binder layer.

SUMMARY OF THE INVENTION

In accordance with the instant invention, the required control of the bulk geometry is attained by employing a binder or a matrix material in particulate form and physically mixing the particulate binder material with a particulate photoconductive material having a certain critically controlled size range. The matrix material and photoconductor particles are then formed into a permanent binder layer by fusing or melting the binder particles together in any convenient manner to form a binder layer in which the dispersion of photoconductor particles is characterized by continuous paths of contacting photoconductor particles contained in the resin binder matrix. By controlling the geometry of the binder layer in accordance with the instant invention, greatly improved mechanical flexibility can be attained for xerographic binder layers. This is

due to extremely low photoconductor concentrations which result in the film or binder layer exhibiting substantially the mechanical properties of the resin or binder matrix inasmuch as the binder constitutes a major portion of the layer. In addition, free standing films or self-supporting binder layers may be easily fabricated inasmuch as binder materials can be selected which have the desired flexibility and strength to be used without the necessity of a supporting substrate or backing. The instant invention also allows for a wider choice of both the binder material, which may be used in order to achieve any desired physical property, as well as photoconductor materials having relatively low resistivities. In addition to the advantages in mechanical properties, the instant invention obviates the disadvantages of cyclic fatigue characteristics which are an inherent problem in the general binder systems described above. The instant invention therefore eliminates the necessity to compromise between the mechanical and electrical properties of a xerographic binder layer, making these essentially independently controlled parameters.

The present invention is especially suitable for producing a photoconductive binder structure for employment in a multiple use high-speed xerographic machine. By employing an extremely low volume concentration of photoconductor particles and by carefully controlling the particle size of the photoconductor and particulate binder material, the orientation of the photoconductor particles in the binder layer may be preselected so as to form continuous photoconductive paths through the thickness of the binder layer. More specifically, binder materials of this invention are used in a particulate form having a restricted mean diameter and size distribution in relationship to the photoconductive particles. A mixture of these particles in the proper proportion can then be dispersed in a suitable fluid carrier medium in which neither the binder nor photoconductor is soluble. A continuous film may then be formed by coating a substrate with this dispersion, removing the fluid carrier, and coalescing the binder particles together by the application of heat and/or pressure, the vapors of a suitable solvent, or by any other suitable method. The final binder layer is characterized by the major portion of the photoconductive particles being arranged in the form of continuous paths throughout a substantially continuous matrix of the binder material.

An important step in the instant invention involves the photoconductor geometry control which is achieved by employing a particulate binder material having a correct size distribution. The instant concept may be illustrated by the following example:

A photoconductive binder layer is made by forming a particulate mixture of photoconductive particles having a size distribution of about 0.001 to 2.0 microns with a thermoplastic resin binder having a particle size distribution of about 1 to 70 microns. The photoconductor is present in a concentration from about 1 to 25 percent by volume. The mixture is dispersed in a suitable fluid carrier in which neither the photoconductor nor binder is soluble. The dispersion is coated onto a metal substrate and the carrier fluid allowed to evaporate. The dried layer is then heated to fuse the binder particles into a binder matrix containing photoconductor particles in the form of continuous paths in particle-to-particle contact throughout the thickness of the

binder layer. The size of the resin particles should, in general, be at least about 5 times that of the photoconductor particles. It should be noted that if the particle size of the photoconductor approaches that of the binder, the desired geometry of the photoconductor particles cannot be achieved and the photoconductor particles become completely encased in the binder matrix. In this case, the desirable results of the applicant's invention are not achieved, as will be shown later.

Binder layers of the controlled dispersion type described above exhibit a combination of electrical characteristics and mechanical properties which are superior to those of the binder systems of the uniform dispersion type as exemplified by the examples described in the Middleton et al. patent.

BRIEF DESCRIPTION OF THE DRAWINGS

In general, the advantages of the improved structure and method in the instant invention will become apparent upon consideration of the following disclosure of the invention; especially when taken in conjunction with the accompanying drawings wherein:

FIG. 1 represents a plot of xerographic sensitivity vs. photoconductor volume concentration for a conventional uniform dispersion xerographic resin binder layer.

FIG. 2A, 2B, 2C, and 2D represent schematic models of a conventional uniform dispersion photoconductive binder layer at various concentrations of photoconductor.

FIG. 3A and 3B represent schematic models of a controlled dispersion photoconductive binder layer according to the invention at various concentrations of photoconductor.

FIG. 4 represents a plot of pore volume vs. the ratio of the smallest to largest matrix particle size in a controlled dispersion binder layer according to this invention.

FIG. 5A is a schematic illustration of a uniform dispersion photoconductive binder structure.

FIG. 5B illustrates a typical uniform dispersion used in forming the structure of FIG. 5A.

FIG. 6A illustrates one embodiment of a controlled dispersion photoconductive binder structure according to the instant invention.

FIG. 6B illustrates one embodiment of a particulate dispersion for forming the controlled dispersion structure of 6A.

FIG. 7 illustrates electrical discharge curves for the structures of FIG. 5A and 6A.

DETAILED DESCRIPTION OF THE DRAWINGS

It can be seen from the foregoing discussion of the conventional binder systems known to the art that the optimum concentration of the photoconductor is a necessary compromise between the electrical characteristics and mechanical properties. If, for example, the sensitivity $E_{.25}$ [defined as the reciprocal of the energy required to discharge 25 percent of the initial voltage $E_{.25} = (1/It) (0.25 V_0)$] of such a system is measured as a function of the volume concentration of a uniformly dispersed photoconductor, then the results illustrated by FIG. 1 are obtained.

The data shown in FIG. 1 represents the variation in sensitivity of a series of binder layers of a cadmium sulfoselenide photoconductor having a maximum particle size of about 0.8 microns dispersed in a matrix of isobu-

tyl methacrylate resin formed from a solution of toluene. It can be seen that some low order photosensitivity is obtained at photoconductor volume concentrations as low as 10 percent, but that the magnitude of response increases rapidly from 25 to 50 percent by volume, above which there is little further increase. The optimum photoconductor concentration for this system in terms of photoresponse rate is therefore about 45 percent by volume or 80 percent by weight. The residual potential level decreases as a function of the photoconductor volume loading in much the same way that the sensitivity increases, such that at 10 percent volume loading the true residual is approximately 80 percent of the initial potential, while at 45 percent loading it has fallen to 5 percent of the initial potential. However, at a 45 percent by volume photoconductor concentration, the resultant coatings tend to be very porous and exhibit an extremely low resistance to abrasion. Therefore, notwithstanding the fact that the discharge characteristics of the system in terms of photoresponse rate and residual potential level are adequate for operation in a high speed xerographic imaging mode, the resultant porosity and poor abrasion resistance result in severe image deterioration with cycling after the initial image has been formed. In addition, undesirably high fatigue, and in many cases, high background levels with partial exposure or solid area development systems are also exhibited with these high volume loadings. Since high surface gloss is lost, and porosity begins to develop above a volume concentration of about 25 percent photoconductor, a large sacrifice in photoresponse rate is necessary to completely alleviate these latter effects. In addition, at this concentration the background potential is appreciable, and although in a single copy imaging mode the voltage can be biased out in the development system, in a cyclic xerographic imaging system the background potential increases with each cycle, resulting in a loss in electrostatic contrast and image deterioration.

The effects shown in FIG. 1 can be further illustrated by envisioning a resin layer of arbitrary thickness coated onto a conductive substrate into which photoconductor particles may be substituted for an equal volume of resin. In FIG. 2A the photoconductor particles are shown as black cubes for the sake of simplicity. If, as in 2A, 10 percent by volume of the resin is replaced by photoconductor, and assuming theoretically perfectly uniform dispersion and no charge transport within the resin, the only photoconductivity which can occur results from the movement of carriers within the photoconductor.

Again assuming a perfectly uniform dispersion, the photoconductor volume concentration can be increased substantially up to 25 percent without resulting in contact between any two or more particles (FIG. 2B). Ignoring surface tension and two-phase boundary effects and assuming particles of cubic shape, any further increase in volume loading above this 25 percent level will result in some particle-to-particle contact, and in the beginning of the formation of continuous pathways through photoconductive particles. For example, in FIG. 2C, increasing the photoconductor volume concentration still further to 30 percent results in the formation of a considerable number of particle contacts, thereby forming a number of continuous particle contacts or pathways which extend from the top surface of the binder layer down to the conductive sub-

strate. The photoresponse rate and the residual potential of the layer are directly related to the number and length of these pathways per unit surface area. Carriers generated by absorbed light must be able to move in the direction of the applied field which is normal to the layer surface and cannot move in the resin except in that special case where the matrix resin is of a specialized type which can support carrier transport. It is therefore not surprising that the photoresponse of these layers increases rapidly above 25 percent volume concentration of photoconductor. Since in reality perfectly uniform dispersion is impossible to attain, there is always some mathematical probability that two or more individual particles will be in contact at any volume concentration, and therefore some low order photosensitivity will be expected at low volume loadings below 25 percent, as illustrated by the experimental data of FIG. 1.

If the photoconductor volume concentration is increased further to 50 percent, every photoconductor particle will be in contact with 12 other particles, assuming perfectly uniform dispersion and cubic particles of uniform size. The maximum number of continuous electronic pathways are thus formed at this concentration, and any further increase in this concentration will not result in an increase in the photoresponse rate or a decrease in the residual level. This effect is again substantiated by the experimental data shown in FIG. 1. It is clear that in forming the maximum number of pathways in this manner that the mechanical properties of the matrix resin cannot be maintained.

It can be seen from FIG. 2D that a considerable number of photoconductor particles are useful only in regard to achieving the maximum continuous path geometry, and in an electronic sense, provide only duplicate or alternate carrier pathways. This effect is illustrated in FIG. 3A where 10 percent by volume of the 50 percent volume concentration layer is replaced by relatively large cubes of pure matrix resin. This reduces the photoconductor concentration and improves the mechanical properties of the layer without detrimentally affecting the number of pathways in the light absorption region, and without destroying the electrical connection of each of the particles in this region to the substrate. In the same way additional cubes of resin may be inserted to bring the total photoconductor concentration down to 10 percent by volume, as shown by FIG. 3B, again without affecting the photoresponse rate and residual level, since the continuity of the paths is not completely broken, nor are the number of paths per unit surface area significantly reduced in the light absorption region. It can be seen, therefore, that high photoresponse rates and low residual levels can be attained in these systems at photoconductor concentrations which are sufficiently low to have little detrimental affect on the physical characteristics of the matrix resin, if the bulk geometry of the layer can be controlled in such a way as to achieve these continuous electronic pathways through the bulk of the layer. According to the instant invention, this controlled geometry is achieved by utilizing the matrix resin in particulate form and photoconductor particles significantly smaller in size than the resin particles, thereby forcing the photoconductor to occupy the interstitial space of the packed resin particles. This concept may be illustrated by the following example:

A coating cast from a dispersion of spherical matrix particles may be thought of as a system of closely packed spheres. The interstitial volume of such a layer will depend therefore on the size distribution of the particles and the type of packing. Hexagonal close packing of monospheres would result, therefore, in an interstitial volume of 47 percent of the total volume. Monospheres of a photoconductor material can be used to fill this 47 percent pore space without affecting the total volume, if the diameter of the photoconductor particle is sufficiently small in comparison to the diameter of the resin particles. If the packing of these photoconductor particles in the matrix pore space is also hexagonal-close-packed, the interstitial volume of the photoconductor will be in turn 47 percent of the total matrix interstitial volume. Since in this example approximately 50 percent of the layer volume comprises matrix particles, and 50 percent of the remaining volume is filled with photoconductor, a photoconductor volume concentration of about 25 percent of the initial layer volume will result. After evaporation of the carrier liquid and coalescence of the binder particles, such as by heating, the volume concentration of the photoconductor particles in the layer is 33 percent. More importantly, in this situation all of the photoconductor particles are in electrical contact from the top surface of the layer to the substrate in the same manner as achieved at 50 percent volume loading in the uniform dispersion case (FIG. 2D). This amounts to a reduction in required photoconductor volume concentration of 33 percent.

The concentration of photoconductor necessary to form continuous electronic pathways is therefore dependent on the interstitial volume of the matrix which is in turn critically dependent on the frequency of matrix particles of varying size and the magnitude of the size distribution as well as the particle shape. FIG. 4 illustrates the former effect where the pore volume can be reduced to about 17, 5, and 3 percent by utilizing matrix particles of vastly differing size having two three four components, respectively. In these cases only about 8.5, 2.5, and 1.5 percent, respectively, by volume photoconductor would be necessary to form the desired continuous electronic pathways. FIG. 4 also illustrates that a low interstitial volume is also obtained by increasing the number of different sizes of particles in the distribution. It would therefore be possible in the idealized case to form a matrix system with an interstitial volume of 3 percent (four components) which would require only 1.5 percent by volume photoconductor to achieve the maximum number of continuous pathways. This concentration (1.5 volume percent) would be comparable to a 50 percent volume concentration in the classic uniform dispersion binder system.

Real particulate packing systems are of course much more complex since seldom are the individual particles spherical or for that matter of constant shape, and the frequency of sizes and the magnitude of the size distribution is normally the natural result of the preparation method, i.e., formation or grinding technique. It may also be obvious that in utilizing this particulate matrix geometry control approach in the fabrication of photoreceptor devices, the upper limit of particle size for the matrix may not exceed the resolution capability of the xerographic development system to be employed, and that the photoconductor size must be sufficiently

smaller than the smallest matrix particle such that it can occupy the interstitial volume of the packing of this smallest size.

The optimum volume concentration of photoconductor to be employed in fabricating a photoreceptor is dependent therefore on the particle size, magnitude and type of size distribution, particle shape of both photoconductor and matrix, the size difference between the two, and the resolution capabilities of the xerographic development system.

In the practice of fabricating a practical xerographic photoreceptor device it has been determined that a preferred maximum size for matrix particles is about 10 microns. Particles above about 10 microns result in some image background, although a material having a very wide size distribution is not detrimentally affected by a small percentage by number of particles as large as about 70 microns. The lower size limit of the matrix is again defined by the size of the photoconductor to be employed, but in a practical system would be in the range of about 0.1 micron. The range of the photoconductor particle size would in turn be from about 0.001 to 2 microns depending on the magnitude and shape of the size distribution. The minimum photoconductor concentration which might be employed, therefore, would be about 1 percent by volume, and the maximum about 25 percent, with most real materials showing an optimum in electrical, cyclic, and xerographic characteristics in the range of about 3 to 15 percent by volume.

The matrix particles determine the number and spacing of chain or pathway ends per unit area in the light absorption region at the photoconductor surface. As previously stated, the upper limit of the matrix particle size may not exceed the resolution capability of the xerographic development system used in conjunction with plates of the instant invention. Further, the photoconductor size must be enough smaller than the smallest matrix particle to occupy the interstitial volume in a packing of this smallest size. The ratio of the size of the matrix resin particles to the photoconductive particles should therefore be at least about 5 to 1 and preferably about 100 to 1 or greater as can be seen from FIG. 4.

The maximum size of binder particles which may be employed in the instant invention is dependent upon the resolution capabilities of the associated xerographic development system. For example, cascade development as described in U.S. Pat. Nos. 2,618,551, 2,618,552 and 2,638,416, can easily attain a resolution capability of about 15 line pairs per millimeter, which corresponds to a dot approximately 33 microns in diameter. Therefore, the maximum size of binder particles which can be used in forming the matrix should be less than about 33 microns for cascade development. The table below lists five representative development systems with their respective normally achieved resolution capability in line pairs per millimeter and in microns. It should be understood that similar determinations can be made for other xerographic development systems.

TABLE

Development System	Normally Achieved Dot Resolution (line pairs per millimeter)	Normally Achieved Resolution in Microns
Cascade	15	33
Magnetic Brush	20	25
Liquid Gravure	6-7	70
Aqueous	6-10	50
Powder Cloud	60	8

FIG. 5A illustrates a low concentration uniform dispersion type binder plate 10, which comprises a supporting substrate 11, coated with a binder layer 12. Binder layer 12, comprises photoconductive particles 13, uniformly dispersed in a resin matrix 14. The binder layer illustrates a concentration of 10 percent by volume photoconductor contained in a 90 percent by volume resin binder. Assuming perfectly uniform dispersion, each photoconductive particle would be completely encased in the binder. This type of photoconductive binder layer, due to a lack of particle contact of the photoconductive material, is characterized by very low order photosensitivity, combined with high residual potential, and would be incapable of use in cyclic imaging for xerography due to an increase in the residual potential with cycling and a consequential loss of contrast potential. FIG. 5B illustrates the uniform type of dispersion which would be used in forming the layer of FIG. 5A. The dispersion comprises photoconductive particles 13 dispersed in a resin-solvent solution 15 which is coated onto a supporting substrate 11. The resin solvent is then evaporated, resulting in the structure of FIG. 5A. This type of structure is characteristic of the particular binder layers described in the Middleton et al. patent above.

FIG. 6A illustrates one embodiment of a xerographic binder layer 20 of the instant invention and comprises a binder layer 21 supported on substrate 22. The binder layer 21 comprises photoconductive particles 23 dispersed in a nonuniform or controlled manner to form continuous paths throughout the binder layer thickness, contained in a resin matrix material 24. The volume concentration for this illustration is also about 10 percent, (the same as in FIG. 5A), but the structure is formed from an initial dispersion of photoconductive particles having a mean size of 0.5 microns with a distribution of from 0.01 to 0.8 microns and a particulate binder material having a mean size of 5 microns with a distribution of from 1 to 12 microns. This dispersion which is coated onto a supporting substrate, insures that continuous photoconductive paths are formed throughout the binder layer thickness. FIG. 6B illustrates the particulate photoconductor-binder dispersion prior to forming the structure of FIG. 6A. In FIG. 6B, binder particles 24 are considerably larger than photoconductor particles 25 and are dispersed in a liquid carrier (not shown). The dispersion is coated onto a supporting substrate 22 and the liquid carrier evaporated off. The dried layer shown by FIG. 6B results in a series of large binder particles having their interstices filled with relatively smaller photoconductive particles 25. It can be seen by FIG. 6B, which is representative of the instant invention, that the volume occupancy of the photoconductor particles is restricted to the interstices of the larger matrix binder particles. On the other

hand, in the solution binder system (FIG. 5B) no photoconductive particle contact can occur at the 10 percent volume concentration with perfect dispersion. The electrical characteristics of the final binder structures of FIGS. 5A and 6A are characterized by the electrical discharge curves for the two layers which show a significantly improved performance attained by the geometry control binder structure of FIG. 6A.

In order to better illustrate the advantages of the instant invention, a direct comparison of the electrical characteristics of a structure such as that illustrated by the instant invention in FIG. 6A is compared to a uniform dispersion type conventional binder system illustrated by FIG. 5A. Two plates illustrating these types of structures are made using a polysulfone resin and a commercial cadmium sulfoselenide pigment available from Ceramic, Color & Chemical Corporation and designated 1020. The plates are made as follows:

Ninety parts by volume of polysulfone resin in particulate form having a mean particle size of 20 microns and a size distribution of from about 1 to 40 microns is dispersed in a carrier liquid (isopropanol) in which neither the resin or the photoconductor is soluble. Ten parts by volume of the cadmium sulfoselenide photoconductor particles having a mean size of 0.5 microns and a size distribution of from 0.05 to 0.8 microns are mixed with the resin and liquid carrier. A 25 micron film of this dispersion is then cast onto an aluminum substrate. The liquid carrier is evaporated resulting in a structure similar to that illustrated by FIG. 6B. The final binder layer is formed by fusing the resin for 3 minutes by heating to 250°C in order to form a continuous binder coating of the type illustrated in FIG. 6A.

A second binder structure is then made by first forming a resin solution of 90 parts by volume polysulfone in cyclohexanone. Ten parts by volume of the same cadmium sulfoselenide photoconductor particles are then dispersed in the resin solution. A film of this dispersion is then cast onto an aluminum substrate and the solvent allowed to evaporate resulting in a continuous layer having the same thickness as the controlled geometry layer formed above. The film of this dispersion prior to evaporation of the solvent is illustrated by FIG. 5B. The final binder layer, after evaporation of the solvent, is illustrated by FIG. 5A. In this situation, with perfectly uniform dispersion, no photoconductive particles are in contact at the 10 percent volume concentration of photoconductor. Both plates are then each separately tested by charging to a negative potential of 600 volts and exposed to light in order to measure the photodischarge. These discharge curves are illustrated by FIG. 7 for each layer and show a large difference in performance obtained by the plate made according to the controlled dispersion technique of the instant invention. It can be seen that the illumination flux density required to obtain significant discharge for the uniform dispersion layer (7.35×10^{14} ph cm⁻² sec⁻¹) is two orders of magnitude greater than that required for the controlled dispersion layer (7.35×10^{12} ph cm⁻² sec⁻¹). In addition, the tail in the discharge curve in the case of the uniform dispersion is true residual which increases with cycling. It can be seen from FIG. 7 that a significant improvement with regard to electrical characteristics is attained through the use of the controlled dispersion binder layer of the instant invention.

One convenient method of forming binder layers of the instant invention comprises utilizing a thermoplas-

tic particulate resin. which following the formation of the dry layer illustrated in FIG. 6B, is fused to form the structure of FIG. 6A. It should be understood, however, that other suitable methods and techniques which would occur to those versed in the art, may also be employed in forming the final layer. Typical methods include solvent fusing, pressure fusing, the employment of latent solvents, or any or all of these in combination with heat.

The binder layers of the instant invention may utilize any suitable photoconductive material. These include both inorganic and organic photoconductors or mixtures thereof.

Typical inorganic photoconductors suitable for use in the instant invention comprise cadmium sulfide, cadmium sulfo-selenide, cadmium selenide, zinc sulfide, lead oxide, zinc oxide, antimony trisulfide and mixtures thereof. U.S. Pat. No. 3,121,006 to Middleton et al. provides a more complete listing of inorganic photoconductors suitable for use in the instant invention. Inorganic photoconductive glasses may also be used as the photoconductor. Typical materials include vitreous or amorphous selenium, alloys of selenium, with materials such as arsenic, tellurium, thallium, bismuth, sulfur, antimony, and mixtures thereof. Typical organic photoconductors suitable for use in the instant invention include the X-form of metal-free phthalocyanine described in U.S. Pat. No. 3,357,989, anthracene, anthraquinones, and metal and metal-free phthalocyanines.

In addition, various additives, activators, dopants and/or sensitizers may also be used to enhance the photoconductivity of the above photoconductive materials. For example, the addition of halogens to arsenic-selenium alloys is known to increase photosensitivity. Similarly, zinc oxide exhibits enhanced spectral response when sensitized with a suitable dye. It is also well known that increased photosensitivity is obtained when photoconductors such as cadmium sulfide are reacted with a very small amount of an activator material such as copper.

The photoconductor concentrations may vary from as low as about 1 percent by volume to about 25 percent by volume of the binder layer. A photoconductor concentration of about 3 to 15 percent by volume, however, is preferred in that it generally insures the optimum combination of electrical characteristics and mechanical properties.

The matrix material may comprise any electrically insulating resin which can be obtained or made in particulate form, cast into a film from a dispersion, and later processed to form a smooth continuous binder layer. Typical resins include polysulfones, acrylates, polyethylene, styrene, diallylphthalate, polyphenylene sulfide, melamine formaldehyde, epoxies, polyesters, polyvinyl chloride, nylon, polyvinyl fluoride and mixtures thereof. Thermoplastic and thermosetting resins are preferred in that they may be easily formed or coalesced into the final binder layer by simply heating the particulate layer.

The particulate mixture of resin and photoconductor particles are normally dispersed in a fluid carrier such as a liquid in which neither the resin nor photoconductor particles is soluble. Alternatively, the carrier fluid may comprise a gas such as air.

The xerographic plate or member of the instant invention may be in any form such as a flexible belt, flat

plate, or drum. The supporting substrate may be made up preferably of a conductive material such as brass, aluminum, steel, or a conductively coated dielectric or insulator. The substrate may be of any convenient thickness, rigid or flexible, and in any desired form such as a sheet, web, belt, plate, cylinder, drum or the like. It may also comprise other materials such as metallized paper, plastic sheets, coated with a thin layer of metal such as aluminum or copper iodide, or glass coated with a thin layer of chromium or tin oxide. In some instances, if desired, the support may be an electrical insulator or dielectric and charging carried out by techniques well known to the art, such as by simultaneously corona charging both sides of the plate with charges of the opposite polarity. Alternatively, after formation of the binder layer the support member may even be dispensed with entirely.

In general, the thickness of the binder layer should be between about 10 to 80 microns, but thicknesses outside this range may also be used.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples further specifically illustrate the present invention with respect to a method of making a photoconductive binder structure having a controlled geometry. The percentages in the disclosure, examples, and claims are by volume unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of the instant invention. In the examples, the sensitivity is defined by $(1/E)$ 0.5 which is the reciprocal of the energy required to discharge the binder layer to 50 percent of the initial potential.

EXAMPLE I

One part by volume of zinc oxide having an average particle size of about 0.5 and a distribution of from about 0.08 to 0.8 (designated 6426 and available from New Jersey Zinc Co.) is dispersed in a carrier liquid (ethylene glycol) with nine parts by volume of a copolymer of 70 percent isobutyl methacrylate and 30 percent styrene which has been ground and classified to have an average particle size of 5 microns with a distribution of from 1 to 12 microns. A film of the dispersion is then coated onto an aluminum substrate, the carrier liquid is evaporated by heating to 90°C for 10 minutes, and the coating fused to form a dried continuous layer about 18 microns thick by heating for 3 minutes at 175°C. The final product is a xerographic plate which comprises a metal support having a photoconductive binder layer thereon. The plate is corona charged to an initial potential of -400 volts and exhibits a dark discharge rate of 50 volts/second and a $(1/E)$ value of 0.04 (ergs/cm²)⁻¹ for 50 percent discharge at 3,750 Å and 7.35×10^{12} photons/cm²/sec., with a residual voltage of 50 volts. The binder layer is smooth, non-porous, and exhibits high gloss. The mechanical properties in terms of adhesion and abrasion resistance are excellent.

EXAMPLE II

An 18 micron binder layer is made using the same zinc oxide of Example I which is dispersed at nine parts by volume in a solution of toluene containing one part by volume of the same matrix material of Example I. The binder layer is formed by coating the mixture onto

an aluminum substrate and allowing the solvent to evaporate. The plate exhibits a dark discharge rate of 50 volts/sec., a $(1/E)$ value for 50 percent discharge of $0.037 \text{ (ergs/cm}^2\text{)}^{-1}$ and a residual of 50 volts from an initial potential of -400 volts. Although this binder plate exhibits electrical characteristics comparable to the plate of Example I, the binder layer is very porous and shows a matte surface finish. Further, the binder layer exhibits poor adhesion and abrasion resistance. With the photo-induced discharge characteristics of the plates of Examples I and II being substantially identical within experimental error, the Examples illustrate that a factor of nine increase in the resin concentration is possible, utilizing the control geometry approach of Example I.

EXAMPLE III

A second plate is made by the method of Example II, except that the concentration of zinc oxide is reduced to one part by volume which is dispersed in a toluene solution containing nine parts by volume of the resin. This plate is charged and tested as in Examples I and II and exhibits no photosensitivity at this illumination wavelength and flux density.

EXAMPLE IV

Six parts by volume of the X-form of metal free phthalocyanine having an average particle size of 0.1 microns with a distribution of from 0.01 – 0.4 microns is dispersed in a carrier liquid (cyclohexanol) with 94 parts of a polyester resin (available from Goodyear under the tradename Flexclad) which has been ground and classified to have an average particle size of 4 microns with a distribution of from 1 to 10 microns. A film of the dispersion is coated onto an aluminum substrate, the carrier liquid is then evaporated by heating to 60°C , and the coating fused to form a continuous layer 20 microns thick by heating for 2 minutes at 230°C . The plate is corona charged to a potential of $+400$ volts and exhibits a dark discharge rate of 50 volts/sec. and a $(1/E)$ value of 0.05 for 50 percent discharge at 8,000A and 8×10^{12} photons/cm²/sec., with a residual voltage of 10 volts. The layer is non-porous, has high gloss and excellent mechanical properties.

EXAMPLE V

Employing the same materials and photoconductor concentration as in Example IV, a 25 micron binder coating is formed from a uniform dispersion of the photoconductor in a acetone solution of the resin. The plate is tested electrically as in Example IV and shows no evidence of photoconductivity at this illumination wavelength and flux density.

EXAMPLE VI

Employing the same materials and method as in Example V, the photoconductor concentration is increased to 25 percent by volume. The resultant 25 micron binder layer would not accept a significant electrostatic charge due to the high dark conductivity of the photoconductor.

EXAMPLE VII

High purity vitreous selenium (99.999 percent by wt. pure) available from Canadian Copper Refiners is ground in liquid nitrogen to a particle size distribution of 0.5 to 2 microns. Fourteen parts by volume of this

material is dispersed in a carrier liquid (cyclohexanol) with 86 parts by volume of Goodyear Flexclad resin which has been ground and classified to have an average particle size of 4 microns with a distribution of from 1 to 10 microns. A film of this dispersion is coated onto an aluminum substrate, the carrier liquid is evaporated by heating to 60°C , and the coating fused to form a continuous layer 20 microns thick by heating for one minute at 230°C . The plate is corona charged to a potential of $+600$ volts and exhibits a dark discharge rate of 5 volts/sec. and a $(1/E)$ value of 0.05 for 50 percent discharge at 4,000A and 8×10^{12} photons/cm²/sec., with a residual value of 40 volts. This layer exhibits excellent flexibility and adhesion.

EXAMPLE VIII

Employing the same materials and photoconductor concentrations as in Example VII, a 20 micron binder coating is formed from a uniform dispersion of the photoconductor in an acetone solution of the resin. The plate is tested electrically as in Example VII and from $+600$ volts initial potential, the plate shows a true residual of 520 volts.

EXAMPLE IX

One part by volume of a synthesized pure cadmium sulfide having a particle size distribution of 0.005 to 0.4 microns is dispersed in a carrier liquid (ethylene glycol) with nine parts by volume of a copolymer of 70 percent isobutyl methacrylate and 30 percent styrene having an average particle size of 5 microns with a distribution of from 1 to 12 microns. A film of this dispersion is coated onto an aluminum substrate, the carrier liquid evaporated by heating to 90°C for 10 minutes and the coating fused to form a continuous layer 25 microns thick by heating for 3 minutes at 175°C . The plate is corona charged to a potential of -600 volts and exhibits a dark discharge rate of 50 volts/sec. and a $(1/E)$ value of $0.09 \text{ (ergs/cm}^2\text{)}^{-1}$ for 50 percent discharge at 5,000A and 7.35×10^{12} photons/cm²/sec., with a residual voltage of 20 volts. The layer is smooth, non-porous and exhibits high gloss and good mechanical properties with respect to adhesion and abrasion resistance.

EXAMPLE X

Employing the same materials and photoconductor concentration of Example IX a coating is formed from a uniform dispersion of the photoconductor in a toluene solution of the resin. No photoconductivity is observed with this sample at the wavelength and light intensity used to test the layer of Example IX.

EXAMPLE XI

Using the same materials and employing the uniform dispersion and solution resin technique of Example X, the photoconductor concentration is increased to 50 percent by volume. From an initial potential of -600 volts the binder layer exhibits a dark discharge rate of 150 volts/sec. and a $(1/E)$ value of $0.09 \text{ (ergs/cm}^2\text{)}^{-1}$ for 50 percent discharge at 5,000A and 7.35×10^{12} photons/cm²/sec., with a residual of 25 volts. This layer, however, is porous, the surface is matte, and the adhesion and abrasion resistance are extremely poor.

EXAMPLE XII

Eighty-one parts by volume of a copolymer of 70 per-

cent isobutyl methacrylate and 30 percent styrene which has been ground and classified to a mean particle size of 5 microns and a distribution of from 1 to 8 microns is dispersed in a carrier liquid (silicone fluid 2CS, available from Dow Corning) with nine parts of a synthesized cadmium sulfoselenide $CdS_{0.6}Se_{0.4}$ having a particle size ranging from 0.001 to 0.4 microns. A film of this dispersion is cast onto an aluminum substrate, the carrier liquid evaporated by heating for 2 hours at 50°C, and the coating fused to form a continuous layer 55 microns thick by heating for three minutes at 175°C.

The resultant film is smooth and non-porous and exhibits mechanical properties essentially equivalent to unpigmented layers of the matrix resin. The plate is corona charged to an initial potential of -600 volts and exhibits a dark discharge rate of 50 volts/sec. and a $(1/E)$ value of 1.0 $(\text{ergs/cm}^2)^{-1}$ for 50 percent discharge at 5,800A and 8×10^{12} photons/cm²/sec., with a residual potential of 10 volts.

The plate is additionally tested by wrapping the aluminum coated flat plate around a cylindrical aluminum drum blank 4 inches in diameter and 9 inches in length. The plate is then cycled 1,000 times by charging, exposing to a pattern of light to form a latent image, followed by developing with toner particles to form a visible image. The image is then transferred to a sheet of paper and fused to form a permanent copy of the original image. The plate is cycled at speeds up to 10 inches/sec. and exhibits no measurable change in the photo-induced discharge characteristics with cycling. Xerographic images made by the plate show high resolution, good edge definition, and high density. Five 1,000 cycle tests are run on the plate with no evidence of image deterioration or loss in electrical characteristics at the end of 5,000 cycles.

EXAMPLE XIII

Employing the identical materials and concentrations of Example XII, a 55 micron coating is formed from a uniform dispersion of the photoconductor in a toluene solution of the resin. The resultant layer is smooth and non-porous, but from an initial potential of -600 volts, the total contrast which could be developed was 100 volts. This represents a residual voltage of 500 volts which increased with cycling, such that on the third cycle essentially no contrast could be developed.

EXAMPLE XIV

Using the same materials and employing the uniform dispersion in solution resin method of Example XIII, the photoconductor concentration is increased to 50 percent by volume and a binder layer is formed on an aluminum substrate. The resultant 55 micron coating is porous with a matte surface, the adhesion and abrasion resistance of the binder layer are extremely poor.

The plate is corona charged to an initial potential of -600 volts, the dark discharge rate is 500 volts per second and the layer exhibits a $(1/E)$ value of 0.5 $(\text{ergs/cm}^2)^{-1}$ for 50 percent discharge at 5,800A and 8×10^{12} photons/cm²/sec., with a residual of 20 volts. This layer could be initially imaged xerographically as in Example XIII, but subsequent images were of poor and decreasing quality due to the inability to remove residual toner from the porous surface.

EXAMPLE XV

Ninety parts by volume of a Goodyear polyester resin

designated Flexclad PE3177A are ground and classified to yield a mean particle size of 5 microns and a distribution of from 1 to 10 microns are dispersed in a carrier liquid (cyclohexanol) with 10 parts of synthesized cadmium sulfoselenide having a particle size ranging from 0.001 to 0.4 microns. A film of this dispersion is cast onto an aluminum substrate, the carrier liquid is evaporated by heating for 4 hours at 60°C, and the coating fused to form a continuous binder layer 55 microns thick by heating for 3 minutes at 230°C. The resultant coating is with smooth, non-porous, and glossy. It exhibits mechanical properties essentially equivalent to unpigmented layers of the matrix resin and shows very high adhesion, flexibility, and abrasion resistance.

The plate is corona charged to an initial potential of -600 volts, and exhibits a dark discharge rate of 50 volts/sec. and a $(1/E)$ value of 0.4 for 50 percent discharge at 5,800A and 8×10^{12} photons/cm²/sec., with a residual potential of 10 volts.

The plate is additionally tested by wrapping the aluminum coated flat plate around a cylindrical aluminum drum blank four inches in diameter and nine inches in length. The plate is then cycled 1,000 times by corona charging, exposing to a pattern of light to form a latent image, followed by developing with toner particles to form a visible image. The image is then transferred to a sheet of paper and fused to form a permanent copy of the original image. The plate is cycled at speeds up to 10 inches/sec. without any measurable change in the photo-induced discharge characteristics with cycling. All of the xerographic images showed high resolution, good edge definition, high density, and low background. No deterioration in electrical characteristics or mechanical properties are observed at the end of cycling.

EXAMPLE XVI

Using the method of Example XV, a second xerographic plate is made using the same materials and ratios as in Example XV, except that the binder layer is formed on a flat stainless steel substrate. The stainless steel substrate coated with the binder layer is then formed in the shape of a metal cylinder four inches in diameter 9 inches long by welding the ends together. The cylinder is placed over a mandrel and cycled in a modified Xerox 813 Office Copier 4,500 times. The images formed from this plate show high resolution, good edge definition, high density and low background. At the end of 4,500 cycles, the plate showed no evidence of image deterioration or loss in electrical characteristics or mechanical properties.

EXAMPLE XVII

Employing the identical materials and concentrations of Example XV, a 55 micron coating is formed from a dispersion of the photoconductor in an acetone solution of the resin. The binder layer is smooth and non-porous, but after corona charging to -600 volts, the plate exhibited a residual voltage of 500 volts and could not be developed after the third cycle due to a loss in contrast potential.

EXAMPLE XVIII

Employing the resin solution, and uniform dispersion technique of Example XVII, the photoconductor concentration was increased to 50 percent by volume. The

resultant 50 micron layer is porous with a matte surface and abrasion resistance is extremely low. From an initial potential of -600 volts the dark discharge rate was 400 volts/sec. and the layer exhibited a $(1/E)$ value of $0.5 \text{ (ergs/cm}^2\text{)}^{-1}$ for 50 percent discharge at 5,800A and 8×10^{12} photons/cm²/sec., with a residual of 20 volts. In addition to poor mechanical properties, this layer could not be operated in a cyclic xerographic imaging system due to high fatigue effects and the inability to remove residual toner from the photoreceptor surface.

Although specific components and proportions have been stated in the above description of the specific embodiments of this invention, other suitable materials and procedures, such as those listed above, may be used with similar results. In addition, other materials may be utilized which synergize, enhance, or otherwise modify the properties of the device of the instant invention.

Other modifications and ramifications of the present invention would appear to those skilled in the art upon reading the disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. A xerographic imaging member which includes a photoconductive insulating layer, said layer comprising an insulating organic resin matrix and a photoconductive material, with substantially all of the photoconductive material in said member in a multiplicity of interlocking photoconductive continuous paths through the thickness of said layer, said photoconductive paths being present in a volume concentration, based on the volume of said layer, of from about 1 to 25 percent, with the outer surface of said layer comprising organic resin material.

2. The layer of claim 1 in which the photoconductive material is present in an amount from about 3 to 15 percent by volume.

3. The layer of claim 1 in which the matrix material is selected from the group consisting of thermoplastic and thermosetting resins.

4. The layer of claim 1 in which the photoconductor comprises an inorganic material.

5. The layer of claim 4 in which the inorganic material comprises a photoconductive glass.

6. The layer of claim 1 in which the photoconductor comprises an inorganic material.

7. The layer of claim 1 in which the photoconductor comprises a material selected from the group consisting of cadmium sulfide, cadmium sulfoselenide, zinc oxide, vitreous selenium, and the X-form of metal-free phthalocyanine.

8. The layer of claim 1 in which the photoconductor comprises cadmium sulfoselenide.

9. The layer of claim 1 in which the resin comprises a material selected from the group consisting of polysulfones, acrylates, polyethylene, styrene, diallylphthalate, polyphenylene sulfide, melamine formaldehyde, epoxies, polyesters, polyvinyl chloride, nylon, polyvinyl fluoride, and mixtures thereof.

10. The layer of claim 1 in which the resin material comprises a polyester and the photoconductor comprises cadmium sulfoselenide.

11. A xerographic imaging member which includes a

supporting substrate having thereon a photoconductive insulating layer, said layer comprising an insulating organic resin matrix containing therein photoconductive particles, with substantially all of the photoconductive particles being in substantial particle-to-particle contact in said member in a multiplicity of interlocking photoconductive paths through the thickness of said layer, said photoconductive paths being present in a volume concentration, based on the volume of said layer, of from about 1 to 25 percent, with the outer surface of said layer comprising organic resin material.

12. The member of claim 11 in which the photoconductor is present in an amount from about 3 to 15 percent by volume.

13. The member of claim 11 in which the resin comprises a polyester, and the photoconductor comprises cadmium sulfoselenide.

14. A method of imaging which comprises:

- a. providing a xerographic imaging member which includes a photoconductive insulating layer, said layer comprising an insulating organic resin matrix and a photoconductive material, with substantially all of the photoconductive material in said member in a multiplicity of interlocking photoconductive continuous paths through the thickness of said layer, said photoconductive paths being present in a volume concentration, based on the volume of said layer, of from about 1 to 25 percent, with the outer surface of said layer comprising organic resin material,
- b. forming a latent electrostatic image on at least one surface of said layer, and
- c. developing said latent electrostatic image to form a visible image.

15. The method of claim 14 in which the photoconductive particles are present in an amount from about 3 to 15 percent by volume.

16. A method of imaging which comprises:

- a. providing a xerographic imaging member which includes a photoconductive insulating layer, said layer comprising an insulating organic resin matrix and a photoconductive material, with substantially all of the photoconductive material in said member in a multiplicity of interlocking photoconductive continuous paths through the thickness of said layer, said photoconductive paths being present in a volume concentration, based on the volume of said layer, of from about 1 to 25 percent, with the outer surface of said layer comprising organic resin material,
- b. uniformly electrostatically charging the surface of said layer,
- c. exposing said layer to a source of activating radiation to form a latent electrostatic image, and
- d. developing said latent image to form a visible image.

17. The plate of claim 16 in which the photoconductor is present in an amount from about 3 to 15 percent by volume.

18. The method of claim 16 in which the imaging steps (b), (c) and (d) are repeated at least one additional time.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,787,208 Dated January 22, 1974

Inventor(s) Robert N. Jones

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

In column 7, line 40, after "two" insert --,-- and after "three" insert --and--.

In column 9, line 5; delete "Dot" from the second table heading and insert --Dot-- after "Achieved" in the third table heading.

In column 13, line 4, delete "em²" and insert --cm²--.

In column 15, line 6, insert --(-- before "CdS_{0.6}Se_{0.4})".

In column 15, line 18, delete "5,8000A" and substitute therefor --5,800A--.

In column 16, line 11, delete "with" and substitute therefor --very--.

In column 16, line 19, delete "5,8000A" and substitute therefor --5,800A--.

In column 17, line 47, in Claim 6, delete "inorganic" and substitute therefor --organic--.

Signed and sealed this 12th day of November 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents