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Jones

[11] **3,909,261**

[45] **Sept. 30, 1975**

[54] **XEROGRAPHIC IMAGING MEMBER HAVING PHOTOCONDUCTIVE MATERIAL IN INTERLOCKING CONTINUOUS PATHS**

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[73] Assignee: **Xerox Corporation,** Stamford, Conn.

[22] Filed: **Dec. 26, 1973**

[21] Appl. No.: **427,767**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 75,390, Sept. 25, 1970, Pat. No. 3,787,208, which is a continuation-in-part of Ser. No. 627,664, April 3, 1967, abandoned.

[52] **U.S. Cl.** ..... **96/1.5;** 96/1 PC; 96/1.8; 117/34; 117/201

[51] **Int. Cl.**[2] **G03G 5/05**

[58] **Field of Search** ..... 96/1.5, 1 PC, 1.8

[56] **References Cited**

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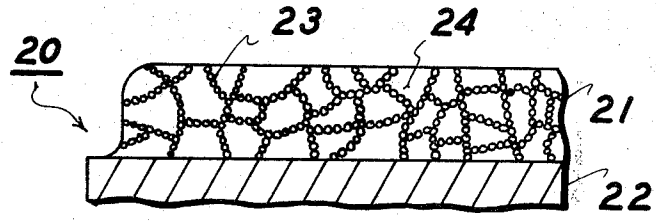
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Primary Examiner—Norman G. Torchin
Assistant Examiner—John R. Miller

[57] **ABSTRACT**

A xerographic imaging member is disclosed which includes a photoconductive insulating layer, said layer comprising an electrically insulating organic resin matrix and a photoconductive material in the form of a matrix of electrically active organic material containing finely divided photoconductive particles therein, with substantially all of the photoconductive material in said member in the form of a multiplicity of interlocking photoconductive continuous paths through the thickness of said layer. The photoconductive paths are present in a volume concentration of from about 1 to 25 percent.

8 Claims, 8 Drawing Figures



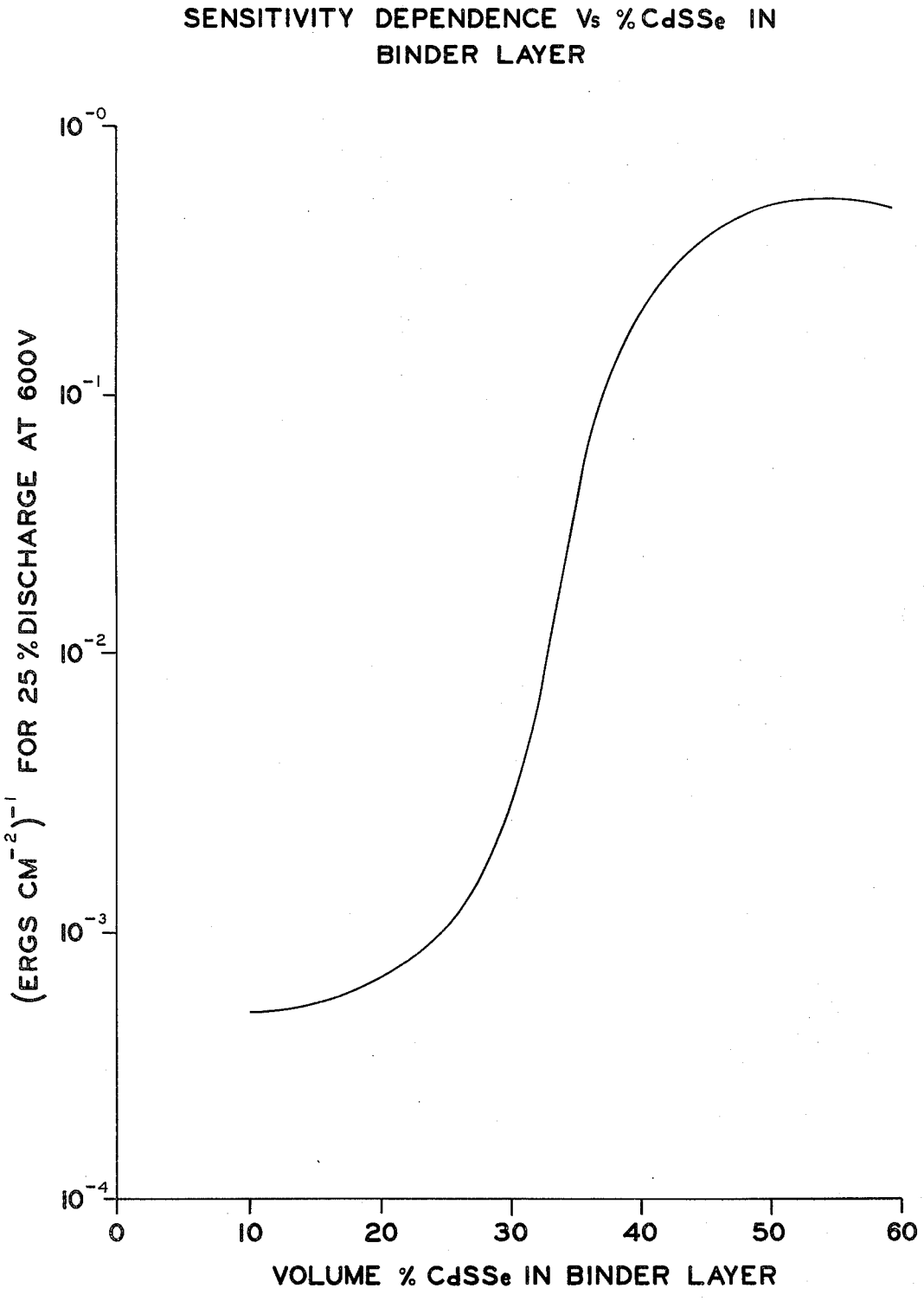
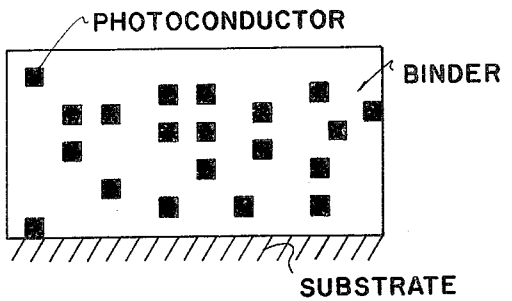
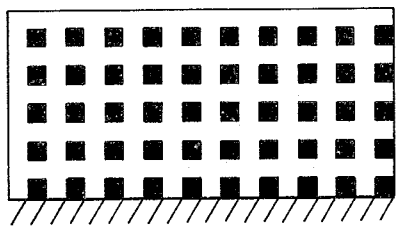

SENSITIVITY DEPENDENCE Vs % CdSSe IN BINDER LAYER
10^{-0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
$(ERGS\ CM^{-2})^{-1}$ FOR 25 % DISCHARGE AT 600V
0
10
20
30
40
50
60
VOLUME % CdSSe IN BINDER LAYER

FIG. 1



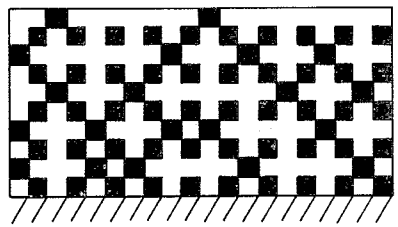
10% VOLUME
PHOTOCONDUCTOR CONCENTRATION

FIG. 2A



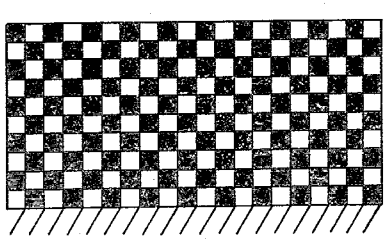
25% VOLUME
PHOTOCONDUCTOR CONCENTRATION

FIG. 2B



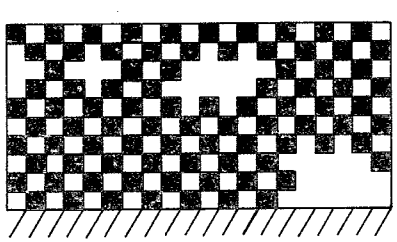
30% VOLUME
PHOTOCONDUCTOR CONCENTRATION

FIG. 2C



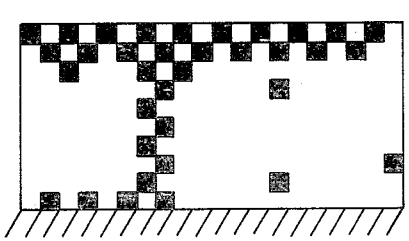
50% VOLUME
PHOTOCONDUCTOR CONCENTRATION

FIG. 3A



10% OF PHOTOCONDUCTOR
VOLUME REPLACED BY LARGE
RESIN PARTICLES

FIG. 3B



40% OF PHOTOCONDUCTOR
VOLUME REPLACED BY LARGE
RESIN PARTICLES

FIG. 3C

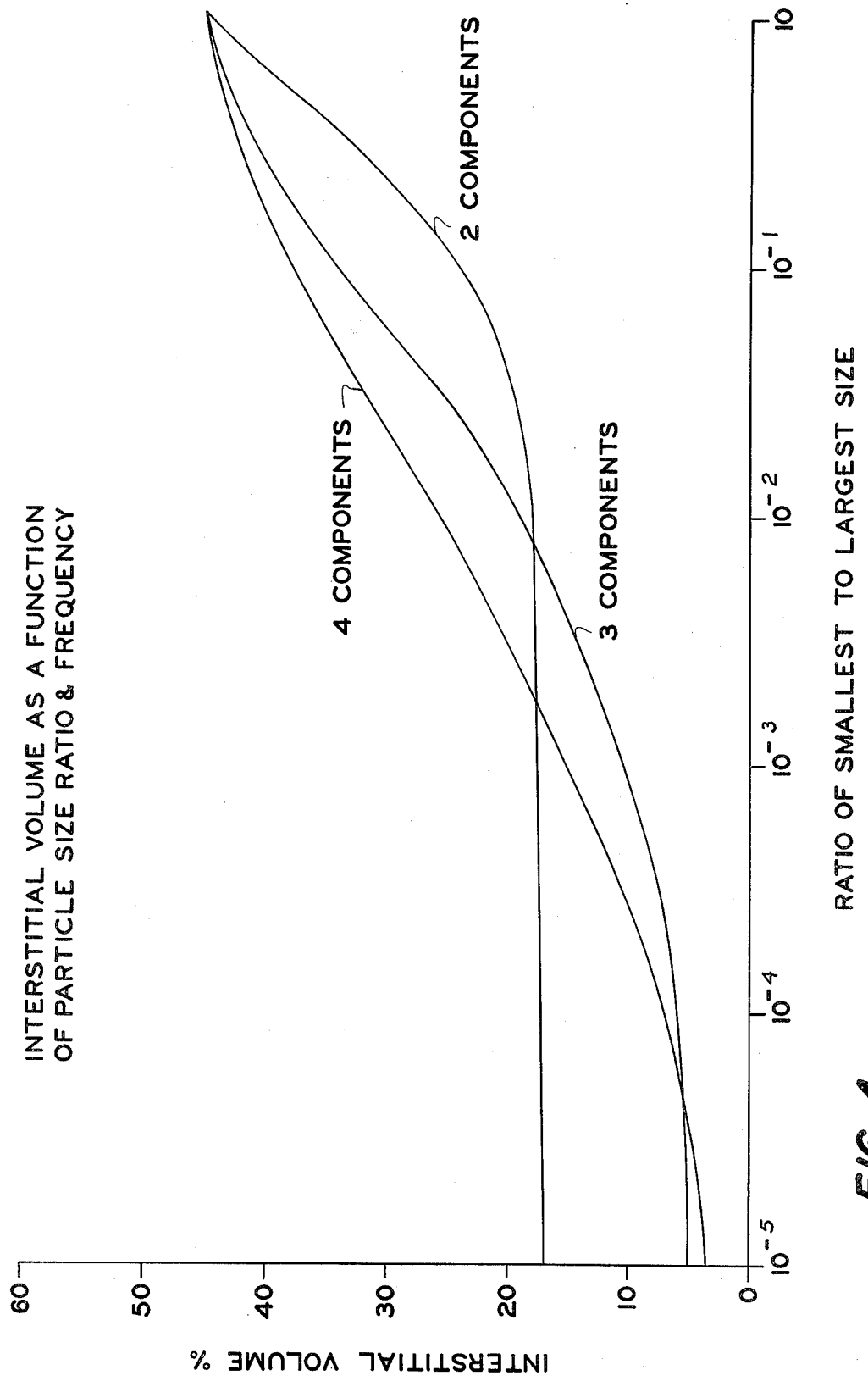

INTERSTITIAL VOLUME AS A FUNCTION
OF PARTICLE SIZE RATIO & FREQUENCY
INTERSTITIAL VOLUME %
60
50
40
30
20
10
0
4 COMPONENTS
3 COMPONENTS
2 COMPONENTS
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10
RATIO OF SMALLEST TO LARGEST SIZE

FIG. 4

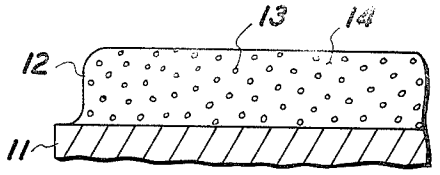


FIG. 5A

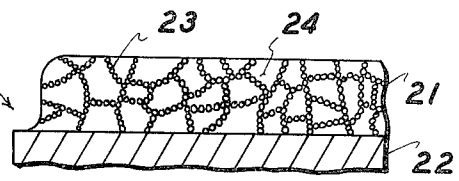


FIG. 6A

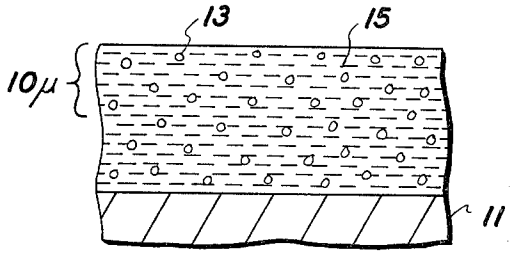


FIG. 5B

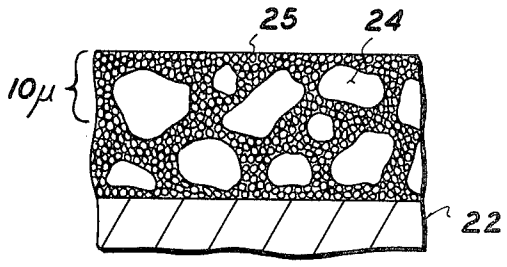


FIG. 6B

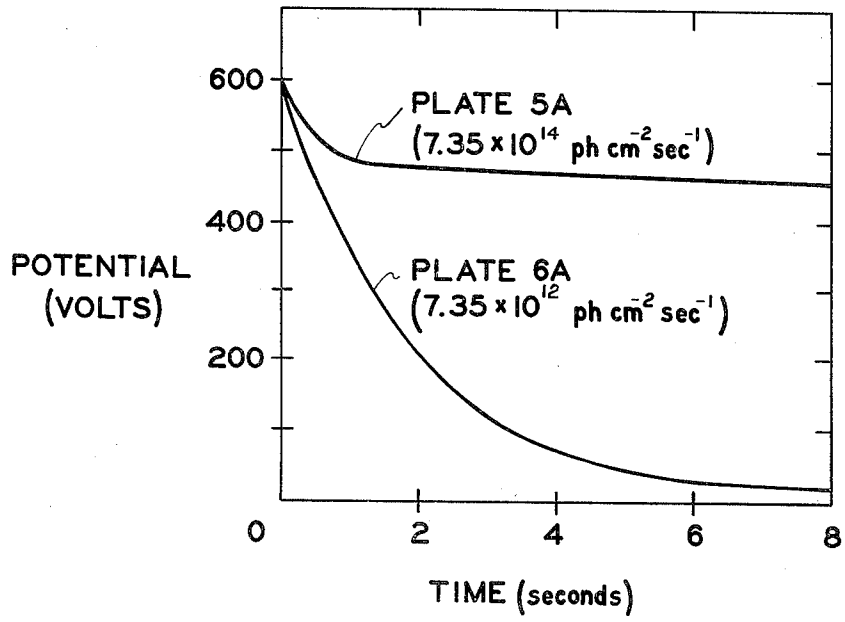


FIG. 7

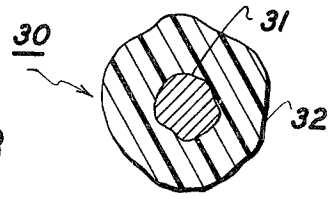


FIG. 8

XEROGRAPHIC IMAGING MEMBER HAVING PHOTOCONDUCTIVE MATERIAL IN INTERLOCKING CONTINUOUS PATHS

RELATED APPLICATIONS

This application is a continuation-in-part of applicant's copending application, Ser. No. 75,390, filed Sept. 25, 1970 now U.S. Pat. No. 3,787,208, which is a continuation-in-part of 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 photoconductive binder layer employing novel composite photoconductive particles.

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 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 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**.

FIG. **8** illustrates an alternative embodiment of a composite photoconductive particle suitable for use in the present invention.

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 $E_{0.25}$ [defined as the reciprocal of the energy required to discharge 25 percent of the initial voltage $E_{.25} = (1/IT)(0.25\ V_o)$] 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 isobutyl 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 between 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 substrate. 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 coalesence 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, and 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 (4 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 comparible 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 .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 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 continous 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 0.0l 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 three 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 sulfoselenide, 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, diallyphthalate, 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.

In an alternative embodiment of the present invention a composite photoconductive particle is used in place of the substantially homogeneous photoconductive particles described above. As illustrated in FIG. **8** of the drawings, this composite photoconductive particle **30,** comprises a small particle or core of substantially homogeneous photoconductive material **31** surrounded by an outer layer or shell of electrically active organic material **32.** FIG. **8** illustrates the situation where a single photoconductive particle is centered within an outer shell of active organic material. It should be understood that more than one photoconductive particle may be contained within the organic shell and that the photoconductive particle or particles need not be in the center of the shell. In addition, the shape of the composite photoconductive particle may be substantially spherical, as illustrated by FIG. **8,** or irregular in shape.

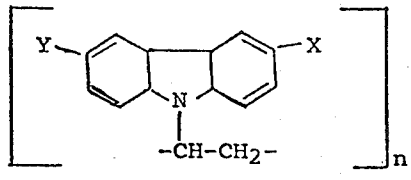
One example of such a composite photoconductive particle comprises a submicron size particle of trigonal selenium surrounded by an outer shell of an organic active material such as polyvinyl carbazole. These composite photoconductive particles are mixed in a solid dispersion with larger insulating resin binder particles using an appropriate dispersion media such as a gas or liquid in which neither the composite photoconductor nor resin binder particles are soluble. The small composite photoconductive particles fill the interstices or void space between the larger binder particles resulting in the formation of continuous conductive paths through the thickness of the binder layer. Following the removal of the dispersion media, the resin matrix particles are coalesced by any suitable technique, as as by heating, resulting in the formation of a substantially continuous insulating matrix containing therein a contiguous network or multiplicity of interlocking photoconductive paths through the binder layer thickness.

Photoconductive material **31** may comprise any organic or inorganic photoconductive material disclosed above with respect to those suitable for use in the imaging member of FIG. **6A.**

The electrically active outer layer **32** may comprise any suitable transparent organic polymer or nonpolymeric material capable of supporting the injection of photo-excited carriers from the photoconductive particle **31,** and allowing the transport of these holes through the organic outer shell to selectively discharge

a surface charge on the exposed surface of the imaging member.

Polymers having these characteristics with respect to photo-excited holes have been found to contain repeating units of a polynuclear aromatic hydrocarbon which may also contain heteratoms such as, for example, nitrogen, oxygen, or sulfur. Typical polymers include poly-N-vinyl carbazole (PVK), poly-1-vinyl pyrene (PVP), poly-9-vinyl anthracene, poly-acenaphthalene, poly-9-(4-pentenyl)-carbazole, poly-9-(5-hexyl)-carbazole, polymethylene pyrene, poly-1-(α-pyrenyl)-butadiene and N-substituted polymeric acrylic acid amides of pyrene. Also included are derivatives of such polymers including alkyl, nitro, amino, halogen, and hydroxy substituted polymers. Typical examples are poly-3-amino carbazole, 1,3-dibromo-poly-N-vinyl carbazole and 3,6-dibromo-poly-N-vinyl carbazole in particular derivatives of the formula:



where X and y are substituents and n is an integer. Also included are structural isomers of these polymers, typical examples include poly-N-vinyl carbazole, poly-2-vinyl carbazole and poly-3-vinyl carbazole. Also included are co-polymers; typical examples are N-vinyl carbazole/methyl acrylate co-polymer and 1-vinyl pyrene/butadiene ABA, and AB block polymers. Typical nonpolymeric materials include carbazole, N-ethylcarbazole, N-phenylcarbazole, pyrene, tetraphene, 1-acetylpyrene, 2,3-benzochrysene, 6,7-benzopyrene, 1-bromopyrene, 1-ethylpyrene, 1-methylpyrene, perylene, 2-phenylindole, tetracene, picene, 1,3,6,8-tetraphenylpyrene, chrysene, fluorene, fluorenone, phenanthrene, triphenylene, 1,2,5,6-dibenzanthracene, 1,2,3,4-dibenzanthracene, 2,3-benzopyrene, anthraquinone, dibenzothiophene, and naphthalene and 1-phenylnaphthalene. The non-polymer materials may also be used in conjunction with either an active polymeric used in conjunction with either an active polymeric material or a non-active polymeric binder. Typical examples include suitable mixtures of carbazole in poly-N-vinyl carbazole as an active polymer and carbazole in a non-active binder. Such non-active binder materials include polycarbonates, acrylate polymers, poly amides, polyesters, polyurethanes, and cellulose polymers

It should be understood that the use of any polymer (a polymer being a large molecule built up by the repetition of small, simple chemical units) whose repeat unit contains the appropriate aromatic hydrocarbon, such as carbazole, and which supports hole injection and transport, may be used. It is not the intent of the invention to restrict the type of polymer which can be employed as the active organic material. Polyesters, polysiloxanes, polyamides, polyurethanes and epoxies as well as block, random or graft co-polymers (containing the aromatic repeat unit) are exemplary of the various types of polymers which can be employed as the active material. In addition suitable mixtures of active polymers with inactive polymers or non-polymeric materials may be employed. One action of certain non-active material is to act as a plasticizer to improve the mechanical properties of the active polymer layer. Typical plasticizers include epoxy resins, polyester resins, polycarbonate resins, 1-phenyl napthalene and chlorinated diphenyl.

Typical materials exhibiting injection and transport properties for electrons include phthalic anhydride, tetrachlorophthalic anhydride, benzil, mellitic anhydride, S-tricyanobenzene, picryl chloride, 2,4-dinitrochlorobenzene, 2,4-dinitrobromobenzene, 4-nitrobiphenyl, 4,4-dinitrobiphenyl, 2,4,6-trinitroanisole, trichlorotrinitrobenzene, trinitro-O-toulene, 4,6-dichloro-1, 3-dinitrobenzene, 4,6-dibromo-1,3-dinitrobenzene, P-dinitrobenzene, chloranil, bromanil, and mixtures thereof. It is further intended to include within the scope of those materials suitable for the active transport layer, other reasonable structural or chemical modifications of the above described materials provided that the modified compound exhibits the desired charge carrier transport characteristics.

While any and all aromatic or heterocyclic electron acceptors having the requisite transparency characteristic are within the purview of the instant invention particularly good electron transport properties are found with aromatic or heterocyclic compounds having more than one substituent of the strong electron withdrawing substituents such as nitro-(—NO_2), sulfonate ion (—SO_3), carboxyl-(—COOH) and cyano-(CN) groupings. From this class of materials, 2,4,7-trinitro-9-fluorenone (TNF), 2,4,5,7-tetranitrofluorenone, trinitroanthracene, dinitroacridene, tetracyanopyrene, and dinitroanthraquinone are preferred materials because of their availability and superior electron transport properties.

These composite photoconductive particles may be made by any suitable method. One typical method comprises dispersing finely divided particles of any suitable photoconductive material in a solution of any suitable active material. The liquid solvent is evaporated and the solid active material dispersed with photoconductive particles is then milled into fine particles which comprise a composite of an inner core comprising a photoconductive particle(s) surrounded by an outer shell of the active material. Another suitable method comprises dispersing the photoconductive particles in a solution of the active material and spray drying the dispersion to the desired particle size by methods well known in the art.

In general, all of the conditions described above for homogeneous photoconductive particles apply for the use of the composite photoconductive particles in this embodiment of the invention.

In forming the binder structures of the present invention, the softening points of the electrically insulating matrix resin and the active organic material may be substantially different. One requirement, however, is that in order to insure the desired final structure or geometry control, the matrix resin and active material should not be miscible or soluble in each other to any significant degree. It should also be understood that the photoconductive paths in this embodiment of the invention may comprise either composite photoconductive particles in substantial particle-to-particle contact or substantially continuous paths comprising the active organic material which has coalesced into substantially

continuous paths having the photoconductive particles contained within the paths.

The mechanism of charge transport using composite photoconductive particle in the form of continuous chains in the binder layer is believed to be as follows. The active organic material is chosen so that it is substantially transparent to the imaging light which is usually in a visible region of the spectrum. The active material, however, has the capability of accepting the injection of photoexcited carriers and allowing transport of these charged carriers through the active layer. In operation, the imaging member containing the photoconductive chains through the binder layer thickness is uniformly electrostatically charged. The imaging member is then exposed to a pattern of activating radiation generally in the visible region which results in the generation of electron-hole pairs by the photoconductive core portion of the composite photoconductor. The mobile carriers formed by exposure to light are injected into and transported through the active organic material to selectively discharge surface charge, resulting in the formation of a latent electrostatic image.

The advantages of the present invention are such that in using a composite photoconductive particle comprising a significant portion of active organic material, there is a further increase in the total concentration or amount of organic material comprising the entire imaging member. It can thus be seen that in this embodiment of the present invention the amount of photoconductive material can be greatly reduced from those embodiments which use homogeneous photoconductive particles. This reduction in the concentration of photoconductive material results in improved mechanical properties in that the imaging member comprises essentially all organic material.

The composite photoconductive particles are used in the same volume concentration as the substantially homogeneous photoconductive particles described above. The concentration of the photoconductive particle component of the composite particles may comprise any volume concentration from about 1 percent by volume up to about 99 percent by volume. It can be seen that the composite configuration would become essentially a homogeneous photoconductive particle as the concentration of the photoconductive particle component approaches 100 percent by volume. The lower the concentration of the photoconductive particle component, the greater the possible improvement in the mechanical properties, therefore a concentration of 1 to 50 percent by volume is preferred.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples further specifically illustrate the present invention with respect to the use of the composite photoconductive particles in a controlled geometric binder layer. 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.

EXAMPLE I

Composite photoconductive particles suitable for use in the present invention are made by the following technique: A polymer solution is prepared by dissolving 70 grams of n-polyvinyl carbazole (PVK), Luvican M-170 grade, available from BASF in 416 grams of toluene and 46 grams of cyclohexanone, 30 grams of trigonal selenium having a particle size of about 300 Angstrom Units (0.003 microns) (also known as hexagonal selenium) is dispersed in the PVK solution. The solution is ball milled for 30 minutes in order to uniformly disperse the trigonal selenium particles in the PVK solution. The solution is then dried to evaporate off the toluene-cyclohexanone solvent resulting in a dried mass which includes solid polyvinyl carbazole having dispersed therein finely divided particles of trigonal selenium. The dried mixture is then ground in a fluid enerty mill to reduce the mean particle size of the composite to about 0.5 microns. These composite particles are characterized by fine trigonal selenium particles being surrounded by an outer casing of polyvinyl carbazole.

EXAMPLE II

Ten parts by volume of a composite photoconductive particles formed by Example I, having an average particle size of 0.5 microns and a distribution of from about 0.1 to 0.9 microns, is dispersed in a cyclohexanol liquid carrier with 90 parts by volume of polyester resin (available from Goodyear under the tradename Flexclad) which has been ground and classified to have an average particle size of 5 microns and a distribution of from about 1 to 10 microns. The film of the dispersion is coated on an aluminum substrate, the liquid carrier then evaporated by heating to 60°C, and the coating fused to form a continuous layer 20 microns thick by heating for 4 minutes at 165°C.

The resulting binder layer is suitable for use in any conventional electrophotographic process involving charging, exposure and the development of a latent electrostatic image.

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 electrically insulating organic resin matrix and a photoconductive material in the form of a matrix of electrically active organic material containing finely divided photoconductive particles therein, said electrically insulating organic resin matrix and said electrically active organic material being not substantially miscible or soluble in each other, said electrically active organic material being substantially transparent to imaging light, said electrically active organic material capable of accepting injection of photo-excited carriers and allowing transport of said carriers through said material, substantially all of the photoconductive material in said member being in the form of 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 member of claim **1** in which the electrically active material comprises an electron transport material.

3. The member of claim **1** in which the electrically active material comprises a hole transport material.

4. A xerographic imaging member which includes a supporting substrate having thereon a photoconductive insulating layer, said layer comprising an electrically organic resin matrix containing therein photoconductive particles, said photoconductive particles being made up of a core member which comprises at least one photoconductive particle and an outer shell portion which comprises an electrically active organic material, said electrically insulating organic matrix and said electrically active organic material being not substantially miscible or soluble in each other, said electrically active organic material being substantially transparent to imaging light, said electrically active organic material capable of accepting injection of photo-excited carriers and allowing transport of said carriers through said material, substantially all of the photoconductive particles being in substantial particle-to-particle contact in said member in the form of 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 said organic resin material.

5. The member of claim **4** in which the electrically active material comprises an electron transport material.

6. The member of claim **4** in which the electrically active material comprises a hole transport material.

7. A method of imaging which comprises:

a. providing a xerographic imaging member which includes a photoconductive insulating layer, said layer comprising an electrically insulating organic resin matrix and a photoconductive material in the form of a matrix of electrically active organic material containing finely divided photoconductive particles therein, said electrically insulating organic resin matrix and said electrically active organic material being not substantially miscible or soluble in each other, said electrically active organic material being substantially transparent to imaging light, said electrically active organic material capable of accepting injection of photo-excited carriers and allowing transport of said carriers through said material, substantially all of the photoconductive material in said member being in the form of 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 developable latent electrostatic image on said member; and

c. developing said latent image to form a visible image.

8. A method of imaging which comprises:

a. providing a xerographic imaging member which includes a supporting substrate having thereon a photoconductive insulating layer, said layer comprising an electrically insulating organic resin matrix containing therein photoconductive particles, said photoconductive particles being made up of a core member which comprises at least one photoconductive particle and an outer shell portion which comprises an electrically active organic material, said electrically insulating organic resin matrix and said electrically active organic material being not substantially miscible or soluble in each other, said electrically active organic material being substantially transparent to imaging light, said electrically active organic material being capable of accepting injection of photo-excited carriers and allowing transport of said carriers through said material, substantially all of the photoconductive particles being in substantial particle-to-particle contact in said member in the form of 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;

b. uniformly electrostatically charging said member,

c. exposing said member to a pattern of activating radiation to form a latent electrostatic image; and

d. developing said latent image to form a visible image.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,909,261
DATED : September 13, 1975
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:

Column 9, Table, third column, change heading to read --Normally Achieved Dot Resolution in Microns--.

Column 9, line 43, delete "continous" and insert --continuous--.

Column 12, line 53, delete "as", second occurrence.

Column 13, Formula, delete "y" and insert --Y--.

Column 14, line 13, delete "trinitro-O-toulene" and insert --trinitro-O-toluene--.

Column 15, line 10, delete "photoexcited" and insert --photo-excited--.

Signed and Sealed this

twentieth Day of *January 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks