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(54) Electrophotographic imaging member and process including a charge transport layer with high charge carrier mobility

(57) An electrophotographic imaging member including a charge generating layer and a charge transport layer is disclosed, the charge transport layer including a π-conjugated polymeric binder and a charge transport molecule. This imaging member is used in an electrophotographic imaging process.

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Description

The present invention relates to electrophotographic imaging members and more specifically to imaging members having an improved charge transport layer. The present invention further relates to a process for using the imaging members. More particularly, the present invention relates to imaging members for use in high speed printers and printers with miniature photoreceptors.

In the art of electrophotography an electrophotographic plate, or photoreceptor, comprising a photoconductive insulating layer on a conductive layer is imaged by first uniformly electrostatically charging the imaging surface of the photoconductive insulating layer. The plate or photoreceptor is then exposed to a pattern of activating electromagnetic radiation such as light, which selectively dissipates the charge in the illuminated areas of the photoconductive insulating layer while leaving behind an electrostatic latent image in the non-illuminated area. This electrostatic latent image may then be developed to form a visible image by depositing finely divided electroscopic toner particles on the surface of the photoconductive insulating layer. The toner particles may be applied to the surface in dry form or dispersed in a liquid carrier. The resulting visible toner image can be transferred to a suitable receiving member such as paper. This imaging process may be repeated many times with reusable photoconductive insulating layers.

As more advanced, higher speed electrophotographic copiers, duplicators and printers were developed, degradation of image quality was encountered during cycling. Moreover, complex, highly sophisticated, duplicating and printing systems operating at high speeds have placed stringent requirements including narrow operating limits on photoreceptors. For example, the numerous layers found in many modern photoconductive imaging members must be highly flexible, adhere well to adjacent layers, be mechanically compatible with other flexible photoreceptor components, and exhibit predictable electrical characteristics within narrow operating limits to provide excellent toner images over many thousands of cycles.

There is also a need for long service life, flexible photoreceptors in compact imaging machines that employ small diameter support rollers for photoreceptor belt systems compressed into a very confined space. Small diameter support rollers are also highly desirable for simple, reliable copy paper stripping systems which utilize the beam strength of the copy paper to automatically remove copy paper sheets from the surface of a photoreceptor belt after toner image transfer. However, small diameter rollers (e.g., less than about 0.75" (19 mm diameter)), raise the threshold of mechanical performance criteria for photoreceptors to such a high level that spontaneous photoreceptor belt material failure becomes a frequent event for flexible belt photoreceptors.

One type of multilayered photoreceptor that has been employed as a belt in electrophotographic imaging systems comprises a substrate, a conductive layer, a charge blocking layer, a charge generating layer, and a charge transport layer. The charge transport layer often comprises an activating small molecule dispersed or dissolved in a polymeric film forming binder. Generally, the polymeric film forming binder in the transport layer is electrically inactive by itself and becomes electrically active when it contains the activating molecule. The expression "electrically active" means that the material is capable of supporting the injection of either the hole or electron photogenerated charge carriers from the material in the charge generating layer and is capable of allowing the transport of these charge carriers through the electrically active layer in order to discharge a surface charge on the active layer. The multilayered type of photoreceptor may also comprise additional layers such as an anti-curl backing layer, an adhesive layer, and an overcoating layer.

As the electrophotographic art advances, there is a continuing desire for photoreceptors that operate at higher speeds. In order to increase the operational speed of photoreceptors, charge transport layers that operate very rapidly, with charge mobilities higher than 10-5cm2/Vsec, are needed. This requirement is influenced by the additional requirement based on the size of the modern miniature photoreceptors. Since the photoreceptor drums used in the miniature photoreceptors are necessarily small, in order to allow the engine of an imaging machine to be small, the development subsystem therein is resultantly very close to the point of image exposure, thereby reducing the time available for the charges to reach the surface of the active layer.

Thus, in view of the increasing use of and need for miniature photoreceptors for future printers, there is a need for high speed charge transport layers capable of exhibiting carrier mobilities in excess of 10-5cm2/Vsec. High hole mobility of greater than 10-5cm2/Vsec is desirable for charge transporting materials to enable the rapid cycling characteristics of modern photoreceptors. It is known to those skilled in the art that these high mobilities and corresponding charge transport velocities can be achieved by: (1) increasing the content of charge transport molecules in the polymeric binder; and (2) using nonpolarizable polymer binders while retaining a relatively high concentration of transport molecules.

Increasing the loading or content of the small charge transport molecules in the binder may, however, lead to an increased compositional instability, i.e., the small transport molecules may easily crystallize out of the layers. On the other hand, changing the binder polymer to a less polarizable polymer, such as polystyrene, may lead to the degradation of the layer's mechanical integrity and the lowering of its abrasion resistance. Thus, there is a existing need for electrophotographic imaging members comprising charge transport layers capable of exhibiting high speed charge carrier

mobilities that maintain mechanical integrity and can be used in high speed miniature photoreceptors.

It is, therefore, an object of the present invention to provide an improved electrophotographic imaging member which overcomes these and other difficulties encountered in the art.

It is also an object of the present invention to provide an electrophotographic imaging member comprising a charge transport layer which exhibits a high speed charge carrier mobility, and which maintains mechanical integrity.

The foregoing objects have been accomplished in accordance with this invention by providing an electrophotographic imaging member comprising a charge generating layer and a charge transport layer, the charge transport layer comprising a charge transport molecule and a π-conjugated polymeric binder, e.g., one which is solubilized by its substituents. The electrophotographic imaging member may additionally include a conductive layer situated beneath the charge generation layer.

In the electrophotographic imaging member of the present invention, the charge transport layer exhibits a high charge carrier mobility, greater than about 10-5cm2/Vsec, while retaining good mechanical characteristics. The π-conjugated polymers of the present invention should be nonconductive and exhibit charge transporting capability and low polarizability. The charge transport layers of the present invention show hole mobilities between 10-4cm2/Vsec to more than 10-3cm2/Vsec at room temperature with the electric fields typically used in electrophotography.

Thus, the electrophotographic imaging member of the present invention can be used in high speed printers with miniaturized photoreceptors.

The Figure is a graph which illustrates the relationship between hole mobility (cm2/Vsec) and electric field (V/cm).

Electrostatographic imaging members are well known in the art. Electrostatographic imaging members may be prepared by various suitable techniques. Typically, a flexible or rigid substrate is provided having an electrically conductive surface. A charge generating layer is then applied to the electrically conductive surface. A charge blocking layer may be applied to the electrically conductive surface prior to the application of the charge generation layer. If desired, an adhesive layer may be utilized between the charge blocking layer and the charge generating layer. Usually the charge generation layer is applied onto the blocking layer and a charge transport layer is formed on the charge generation layer. However, in some embodiments, the charge transport layer is applied prior to the charge generation layer. The composition comprising the π-conjugated polymers of the present invention and standard charge transport molecules is present in the charge transport layer.

The substrate may be opaque or substantially transparent and may comprise numerous suitable materials having the required mechanical properties. Accordingly, the substrate may comprise a layer of an electrically non-conductive or conductive material such as an inorganic or an organic composition. As electrically nonconducting materials there may be employed various resins known for this purpose including polyesters, polycarbonates, polyamides, polyurethanes, and the like which are flexible as thin webs. The electrically insulating or conductive substrate may be in the form of an endless flexible belt, a web, a rigid cylinder, a sheet and the like.

The thickness of the substrate layer depends on numerous factors, including strength desired and economical considerations. Thus, the substrate layer for a flexible belt may be of substantial thickness, for example, about 200 micrometers, or of minimum thickness less than 50 micrometers, provided there are no adverse effects on the final electrostatographic device. In one flexible belt embodiment, the thickness of this layer ranges from about 65 micrometers to about 150 micrometers, and preferably from about 75 micrometers to about 125 micrometers for optimum flexibility and minimum stretch when cycled around small diameter rollers, e.g., 12 millimeter diameter rollers. The surface of the substrate layer is preferably cleaned prior to coating to promote greater adhesion of the deposited coating. Cleaning may be effected, for example, by exposing the surface of the substrate layer to plasma discharge, ion bombardment and the like.

The conductive layer may vary in thickness over substantially wide ranges depending on the optical transparency and degree of flexibility desired for the electrostatographic member. Accordingly, for a flexible photoresponsive imaging device, the thickness of the conductive layer may be between about 2nm to about 75nm, and more preferably from about 10nm to about 20nm for an optimum combination of electrical conductivity, flexibility and light transmission. The flexible conductive layer may be an electrically conductive metal layer formed, for example, on the substrate by any suitable coating technique, such as a vacuum depositing technique. Typical metals include aluminum, zirconium, niobium, tantalum, vanadium and hafnium, titanium, nickel, stainless steel, chromium, tungsten, molybdenum, and the like. In general, a continuous metal film can be attained on a suitable substrate, e.g. a polyester web substrate such as Mylar™ available from E.I. duPont de Nemours & Co. with magnetron sputtering.

If desired, an alloy of suitable metals may be deposited on the substrate. Typical metal alloys may contain two or more metals such as zirconium, niobium, tantalum, vanadium and hafnium, titanium, nickel, stainless steel, chromium, tungsten, molybdenum, and the like, and mixtures thereof. Regardless of the technique employed to form the metal layer, a thin layer of metal oxide forms on the outer surface of most metals upon exposure to air. Thus, when other layers overlying the metal layer are characterized as "contiguous" layers, it is intended that these overlying contiguous layers may, in fact, contain a thin metal oxide layer that has formed on the outer surface of the oxidizable metal layer. Generally, for rear erase exposure, a conductive layer light transparency of at least about 15 percent is desirable. The

conductive layer need not be limited to metals. Other examples of conductive layers may be combinations of materials such as conductive indium tin oxide as a transparent layer for light having a wavelength between about 400nm and about 700nm or a conductive carbon black dispersed in a plastic binder as an opaque conductive layer. Conventional techniques for applying a conductive layer to the substrate include spraying, dip coating, roll coating, wire wound rod coating, gravure coating, Bird applicator coating, and the like. Drying of the deposited coating may be effected by any suitable conventional technique such as oven drying, infra red radiation drying, air drying and the like. In a drum embodiment, the drum material can be an aluminum cylinder, a plastic rod and the like.

After formation of an electrically conductive surface, a hole blocking layer may be applied thereto for photoreceptors. Generally, electron blocking layers for positively charged photoreceptors allow holes from the imaging surface of the photoreceptor to migrate toward the conductive layer. Any suitable blocking layer capable of forming an electronic barrier to holes between the adjacent photoconductive layer and the underlying conductive layer may be utilized. The blocking layer may be organic or inorganic and may be deposited by any suitable technique. For example, if the blocking layer is soluble in a solvent, it may be applied as a solution and the solvent can subsequently be removed by any conventional method such as by drying. Typical blocking layers include polyvinylbutyral, organosilanes, epoxy resins, polyesters, polyamides, polyurethanes, pyroxyline vinylidene chloride resin, silicone resins, fluorocarbon resins and the like containing an organo metallic salt. Other blocking layer materials include nitrogen containing siloxanes or nitrogen containing titanium compounds such as trimethoxysilyl propylene diamine, hydrolyzed trimethoxysilyl propyl ethylene diamine, N-beta-(aminoethyl) gamma-amino-propyl trimethoxy silane, isopropyl 4-aminobenzene sulfonyl, di (dodecylbenzene sulfonyl) titanate, isopropyl di(4-aminobenzoyl)isostearoyl titanate, isopropyl tri(N-ethylamino-ethylamino)titanate, isopropyl trianthranil titanate, isopropyl tri(N,N-dimethylethylamino)titanate, titanium-4-amino benzene sulfonate oxyacetate, titanium 4-aminobenzoate isostearate oxyacetate, [H2N(CH2)4]CH3Si(OCH3)2, (gamma-aminobutyl) methyl diethoxysilane, and [H2N(CH2)3]CH3Si(OCH3)2 (gamma-aminopropyl) methyl diethoxysilane, as disclosed in US-A-4,291,110, 4,338,387, 4,286,033 and 4,291,110. A preferred blocking layer comprises a reaction product between a hydrolyzed silane and the oxidized surface of a metal ground plane layer. The oxidized surface inherently forms on the outer surface of most metal ground plane layers when exposed to air after deposition. The blocking layer should be continuous and have a thickness of less than about 0.2 micrometer because greater thicknesses may lead to undesirably high residual voltage. A blocking layer of between about 0.005 micrometer and about 0.3 micrometer (5nm-300nm) is preferred because charge neutralization after the exposure step is facilitated and optimum electrical performance is achieved. A thickness of between about 0.3 micrometer and about 0.06 micrometer is preferred for metal oxide layers for optimum electrical behavior. Optimum results are achieved with a siloxane blocking layer. The blocking layer may be applied by any suitable conventional technique such as spraying, dip coating, draw bar coating, gravure coating, silk screening, air knife coating, reverse roll coating, vacuum deposition, chemical treatment and the like. For convenience in obtaining thin layers, the blocking layers are preferably applied in the form of a dilute solution, with the solvent being removed after deposition of the coating by conventional techniques such as by vacuum, heating and the like.

An optional adhesive layer may be applied to the hole blocking layer. Any suitable adhesive layer well known in the art may be utilized. Typical adhesive layer materials include, for example, polyesters, duPont 49,000 (available from E. I. duPont de Nemours and Company), Vitel PE100 (available from Goodyear Tire & Rubber), polyurethanes, and the like. Satisfactory results may be achieved with adhesive layer thickness between about 0.05 micrometer (50nm) and about 0.3 micrometer (300nm). Any suitable solvent or solvent mixtures may be employed to form a coating solution of the adhesive layer material. Typical solvents include tetrahydrofuran, toluene, methylene chloride, cyclohexanone, an the like, and mixtures thereof. Conventional techniques for applying an adhesive layer coating mixture to the charge blocking layer include spraying, dip coating, roll coating, wire wound rod coating, gravure coating, Bird applicator coating, and the like. Drying of the deposited coating may be effected by any suitable conventional technique such as oven drying, infra red radiation drying, air drying and the like.

Any suitable photogenerating layer may be applied to the adhesive or blocking layer which can then be overcoated with a contiguous hole transport layer as described hereinafter. Typical photogenerating layers comprise a resinous binder and a photogenerating composition or pigment. Examples of typical photogenerating layers include inorganic photoconductive particles such as amorphous selenium, trigonal selenium, and selenium alloys selected from the group consisting of selenium-tellurium, selenium-tellurium-arsenic, selenium arsenide and mixtures thereof, and organic photoconductive particles including various phthalocyanine pigments such as the X-form of metal free phthalocyanine described in US-A-3,357,989, metal phthalocyanines such as vanadyl phthalocyanine and copper phthalocyanine, dibromoanthanthrone, squarylium, quinacridones available from DuPont under the tradename Monastral Red, Monastral Violet and Monastral Red Y, Vat Orange 1 and Vat Orange 3 trade names for dibromo anthanthrone pigments, benzimidazole perylene, substituted 2,4-diamino-triazines disclosed in US-A-3,442,781, polynuclear aromatic quinones available from Allied Chemical Corporation under the tradename Indofast Double Scarlet, Indofast Violet Lake b, Indofast Brilliant Scarlet and Indofast Orange, and the like dispersed in a film forming polymeric binder. Selenium, selenium alloy, benzimidazole perylene, and the like and mixtures thereof may be formed as a continuous, homogenous

photogenerating layer. Benzimidazole perylene compositions are well known and described, for example in US-A-4,587,189. Multi-photogenerating layer compositions may be utilized where a photoconductive layer enhances or reduces the properties of the photogenerating layer. Examples of this type of configuration are described in US-A-4,415,639. Other suitable photogenerating materials known in the art may also be utilized, if desired. Charge generating binder layers comprising particles or layers comprising a photoconductive material such as vanadyl phthalocyanine, metal free phthalocyanine, benzimidazole perylene, amorphous selenium, trigonal selenium, selenium alloys such as selenium-tellurium, selenium-tellurium-arsenic, selenium arsenide, and the like and mixtures thereof are especially preferred because of their sensitivity to white light. Vanadyl phthalocyanine, metal free phthalocyanine and tellurium alloys are also preferred because these materials provide the additional benefit of being sensitive to infrared light.

Any suitable polymeric film forming binder material may be employed as the matrix in the photogenerating binder layer. Typical polymeric film forming materials include those described, for example, in US-A-3,121,006. Thus, typical organic polymeric film forming binders include thermoplastic and thermosetting resins such as polycarbonates, polyesters, polyamides, polyurethanes, polystyrenes, polyarylethers, polyarylsulfones, polybutadienes, polysulfones, polyethersulfones, polyethylenes, polypropylenes, polyimides, polymethylpentenes, polyphenylene sulfides, polyvinyl acetate, polysiloxanes, polyacrylates, polyvinyl acetals, polyamides, polyimides, amine resins, phenylene oxide resins, terephthalic acid resins, phenoxy resins, epoxy resins, phenolic resins, polystyrene and acrylonitrile copolymers, polyvinylchloride, vinylchloride and vinyl acetate copolymers, acrylate copolymers, alkyd resins, cellulosic film formers, poly(amideimide), styrene-butadiene copolymers, vinylidenechloride-vinylchloride copolymers, vinylacetate-vinylidenechloride copolymers, styrene-alkyd resins, polyvinylcarbazole, and the like. These polymers may be block, random or alternating copolymers.

Active carrier transporting resin may also be employed as the binder in the photogenerating layer. These resins are particularly useful where the concentration of carrier generating pigment particles is low and the thickness of the carrier generation layer is substantially thicker than about 0.7 micrometer. The active resin commonly used as a binder is polyvinylcarbazole whose function is to transport carriers which would otherwise be trapped in the layer.

The photogenerating composition or pigment is present in the resinous binder composition in various amounts, generally, however, from about 5 percent by volume to about 90 percent by volume of the photogenerating pigment is dispersed in about 10 percent by volume to about 95 percent by volume of the resinous binder, and preferably from about 20 percent by volume to about 30 percent by volume of the photogenerating pigment is dispersed in about 70 percent by volume to about 80 percent by volume of the resinous binder composition. In one embodiment about 8 percent by volume of the photogenerating pigment is dispersed in about 92 percent by volume of the resinous binder composition.

For embodiments in which the photogenerating layers do not contain a resinous binder, the photogenerating layer may comprise any suitable, well known homogeneous photogenerating material. Typical homogenous photogenerating materials include inorganic photoconductive compounds such as amorphous selenium, selenium alloys selected such as selenium-tellurium, selenium-tellurium-arsenic, and selenium arsenide and organic materials such as chlorindium phthalocyanine, chloraluminum phthalocyanine, vanadyl phthalocyanine, and the like.

The photogenerating layer containing photoconductive compositions and/or pigments and the resinous binder material generally ranges in thickness of from about 0.1 micrometer to about 5.0 micrometers, and preferably has a thickness of from about 0.3 micrometer to about 3 micrometers. The photogenerating layer thickness is related to binder content. Higher binder content compositions generally require thicker layers for photogeneration. Thicknesses outside these ranges can be selected providing the objectives of the present invention are achieved.

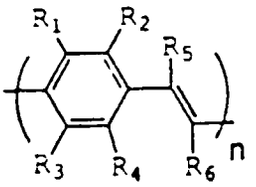
Any suitable and conventional technique may be utilized to mix and thereafter apply the photogenerating layer coating mixture. Typical application techniques include spraying, dip coating, roll coating, wire wound rod coating, and the like. Such coating methods are well known in the art as shown by US-A-4,725,518, 5,037,676 and 5,219,690. Drying of the deposited coating may be effected by any suitable conventional technique such as oven drying, infra red radiation drying, air drying and the like.

The charge transport layer of the present invention comprises a polymeric binder and a charge transport molecule. The charge transport layer of the present invention should be capable of supporting the injection of photogenerated holes from the photogeneration layer to allow the transport of these holes through the transport layer to selectively neutralize the surface charge.

The polymeric binder of the present invention comprises a film-forming π-conjugated polymer. The π-conjugated polymers of the present invention are also capable of transporting injected or photogenerated holes. The π-conjugated polymers of the present invention preferably are insulating and are also preferably solubilized by pendant substituents. The π-conjugated polymers of the present invention are also preferably substituted with substituents that render the polymer soluble in typical organic solvents. In addition, the π-conjugated polymers of the present invention are not only charge transporting but are also tough and flexible.

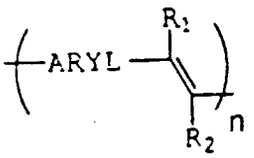
The charge transport layer of the present invention preferably comprises as the π-conjugated polymeric binder a substituted poly(phenylene vinylene). The substituents on the polymer render the poly(phenylene vinylene) soluble in

typical organic solvents. The substituted poly(phenylene vinylene) polymer can be represented by the formula I:

I. 

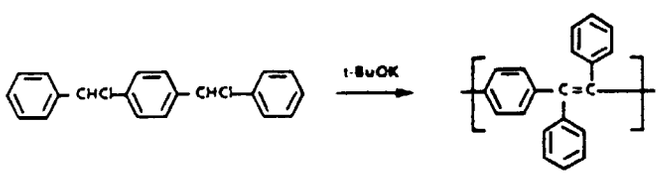
in which:
n is an integer ranging from about 10 to about 10,000; R1, R2, R3, R4, R5 and R6 may each independently represent: hydrogen; an aliphatic group containing from 1 to 16 carbon atoms; an alkoxy group selected from methoxy, ethoxy, propoxy and butoxy; an aromatic group selected from phenyl, mono-, di-, ter-, tetra- and penta- substituted phenyl, wherein each substituent on the aromatic group may be selected from alkyl, p-alkoxy, phenoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl; naphthyl; substituted naphthyl, wherein each substituent on the naphthyl group may be selected from alkyl, p-alkoxy, phenoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl; anthryl; substituted anthryl, wherein each substituent on the anthryl group may be selected from alkyl, p-alkoxy, phenoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl.

Another preferred embodiment of the present invention comprises as the π-conjugated polymeric binder a substituted poly(arylene vinylene). The substituted poly(arylene vinylene) polymers of the invention can be represented by the formula II:

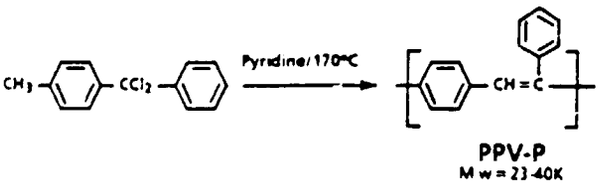
II. 

in which:
n is an integer ranging from about 10 to about 10,000; the aryl is derived from an aromatic group selected from benzene, naphthalene, anthracene, phenanthrene, fluorene, pyrene, perylene, biphenyl and triphenyl. The aryl may be substituted with one or several aliphatic groups containing from 1 to 16 carbon atoms; one or several alkoxy groups selected from methoxy, ethoxy, propoxy, and butoxy; one or several aromatic groups selected from phenyl, mono-, di-, ter-, tetra-, and pentasubstituted phenyl, wherein the substituents on the aromatic group may be the same or different and may be selected from alkyl, p-alkoxy, dialkylamino, diarylamino, N-carbazolyl and benzoyl groups; naphthyl; substituted naphthyl, wherein the substituents on the naphthyl group may be selected from one or more of alkyl, p-alkoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl groups; R1 and R2 may be selected from the group containing hydrogen, aliphatic groups containing 1 to 16 carbon atoms; alkoxy groups such as methoxy, ethoxy, propoxy, butoxy and phenoxy; aromatic groups such as phenyl, mono-, di-, ter-, tetra-, or penta- substituted phenyl, wherein the substituents on the aromatic group are selected from one or more of alkyl, p-alkoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl groups; naphthyl; substituted naphthyl, wherein the substituents on the naphthyl group are selected from one or more of alkyl, p-alkoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl groups; naphthoxy, N-carbazolyl and fluorenyl.

The insulating conjugated polymers of the present invention can be synthesized by methods well-known to those skilled in the art. Exemplary basic synthesis routes of the polymers of the present invention are:



PPV-DP



Additional examples of methods which can be used for the synthesis of polymers similar to those of the present invention can be found in "Synthesis and Photoconductivity of poly(2,7-fluorenylene-1,2-diphenylvinylene)," ACTA POLYMERICA, vol. 37, pp. 369-75 (1986). For a discussion of one method for the synthesis of poly(phenylene vinylenes), see D. Raabe and H. Horhold, "Synthesis of Functionalized poly(1,4-phenylene-1,2-diphenylvinylenes) by Dehydrochlorination of unsymmetric p-xylene dichlorides," ACTA POLYMERICA, vol. 43, pp. 275-78 (1992).

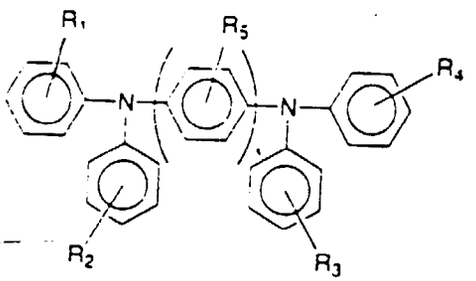
The conjugated polymers of the present invention may be solubilized in a variety of solvents. Any standard solvent, polar or nonpolar, may be used for the polymers of the present invention, as long as the polymers are soluble therein. Standard solvents include benzene, toluene, xylenes, tetrahydrofuran, methylene chloride, chloroform and trichloroethane.

The conjugated polymers of the present invention also allow molecular doping to high levels. In the context of the present invention, high levels include about 40 weight percent or higher, such that the polymers are almost fully miscible with the charge transport molecules, i.e., the "dopants," without phase separation. Without the charge transport molecules, or dopants, the polymers of the present invention, especially the poly(phenylene vinylenes), would transport holes only partially, with a lot of resultant charge trapping, i.e., the holes would not make it through the layer. Preferred levels of molecular doping range from 40 to 60 weight percent.

Charge transporting molecules, or dopants, are also useful as additives dissolved or molecularly dispersed in electrically inactive polymeric materials which cause these materials to become electrically active. Charge transporting molecules are added to polymeric materials which are normally incapable of supporting the injection of photogenerated holes from the generation material and incapable of allowing the transport of these holes therethrough. This converts the electrically inactive polymeric material to a material capable of supporting the injection of photogenerated holes from the generation material and capable of allowing the transport of these holes through the active layer in order to discharge the surface charge on the active layer.

The charge transport layer of the present invention may comprise standard charge transporting molecules. The charge transporting molecules are homogeneously dispersed (dissolved) in the conjugated polymeric binder. The charge transporting molecules are incorporated into the polymeric binder by first forming a homogeneous solution of both components, the binder and the charge transport molecule, in a suitable solvent, followed by casting a film of the solution onto a substrate, and then by allowing the solvent to evaporate.

Preferred charge transporting molecules that may be used in the present invention are molecules of the formula:



in which:
n is an integer ranging from 1 to 4; and R1, R2, R3, R4 and R5 may be selected from hydrogen and an aliphatic or an alkoxy group having from 1 to 12 carbon atoms.

Also preferred, are molecules of the TPD family as well as other suitable hole transport molecules, such as those exemplified in US-A-4,081,274, 4,265,990, 4,273,846, 4,299,897, 4,306,008, 4,346,158 and 4,588,666. Preferred hole transport molecules include TPD {N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[4,4'-biphenyl]-1,1'-diamine}, ETPD {N,N'-bis- (3-methylphenyl)-N,N'-bis(4-ethylphenyl)-[4,4'-bis(3,3'-methyl)biphenyl}-1,1'-diamine, Me-O-TPD {N,N'-dimethyl-N, N'-bis(3-methoxyphenyl)-[4,4'-biphenyl]-1,1'-diamine} and 1,1'-bis((di-4-tolylamino)phenyl]cyclohexane, which was shown to effectively support hole transport in a publication by P. M. Borsenberger, E. H. Magin and J. J. Fitzgerald in

J. PHYS. CHEM. vol. 97, p. 9213 (1993)(This molecule is one of a few that display high hole mobility in other binders also, near 10-5 cm2/Vsec.).

Any suitable solvent or solvent mixture may be employed to form a coating mixture of the charge transport layer material, i.e., the conjugated polymeric binder and hole transport compound. Typical solvents include benzene, toluene, xylenes, tetrahydrofuran, methylene chloride, chloroform, trichloroethane and the like. Any suitable and conventional technique may be utilized to thereafter apply the charge transport layer coating mixture to the charge generating layer. Typical application techniques include spraying, dip coating, roll coating, wire wound rod coating, and the like. Such coating methods are well known in the art as shown by US-A-4,725,518, 5,037,676, and 5,219,690. Drying of the deposited coating may be effected by any suitable conventional technique such as oven drying, infra red radiation drying, air drying the like.

The charge transport molecule is present in the charge transport layer material in an amount ranging from about 5% to about 60% by weight based on the amount of polymeric binder, with a preferred range of about 10% to about 50%, and an optimum range of about 10% to about 30%.

When a conductive layer is present and the charge generating layer is sandwiched between the conductive layer and the charge transport layer, the transport layer not only serves to transport holes, but also protects the charge generating layer from abrasion or chemical attack and therefore extends the operating life of the electrophotographic imaging member. The charge transport layer alone, in the absence of any charge generation layer, should exhibit negligible, if any, discharge when exposed to a wavelength of light useful in xerography, e.g., about 400nm to 900nm. Therefore, the charge transport layer is substantially transparent to radiation in a region in which the photoconductor is to be used. Thus, the charge transport layer is a substantially non-photoconductive material which supports the injection of photogenerated holes from the charge generating layer. The transport layer is normally transparent when exposure is effected through the layer to ensure that most of the incedent radiation is utilized by the underlying charge generating layer for efficient photogeneration.

The thickness of the charge transport layer may range from about 5 to about 60 micrometers, but thicknesses outside this range can also be used. Preferably the thickness ranges from about 10 to about 50 micrometers, and more preferably the thickness ranges from 10 to 30 micrometers. The charge transport layer should be an insulator to the extent that the electrostatic charge placed on the charge transport layer is not conducted in the absence of illumination at a rate sufficient to prevent formation and retention of an electrostatic latent image thereon. In general, the ratio of the thickness of the charge transport layer to the charge generating layer is preferably maintained from about 2:1 to 200:1 and in some instances as great as 400:1. In other words, the charge transport layer, is substantially nonabsorbing to visible light or radiation in the region of intended use but is "active" in that it allows the injection of photogenerated holes from the charge generating layer, and allows these holes to be transported through the charge transport layer to selectively discharge a surface charge on the surface thereof.

Other layers may also be included in the electrophotographic imaging members disclosed herein such as conventional electrically conductive ground strip along one edge of the belt or drum in contact with the conductive layer, blocking layer, adhesive layer or charge generating layer to facilitate connection of the electrically conductive layer of the photoreceptor to ground or to an electrical bias. Ground strips are well known and usually comprise conductive particles dispersed in a film forming binder.

Optionally, an overcoat layer may also be utilized to improve resistance to abrasion. In some cases an anti-curl back coating may be applied to the side opposite the photoreceptor to provide flatness and/or abrasion resistance. These overcoating and anti-curl back coating layers are well known in the art and may comprise thermoplastic organic polymers that are electrically insulating or slightly semi-conductive. Overcoatings are continuous and generally have a thickness of less than about 10 micrometers.

The electrophotographic imaging members of this invention may comprise, for example, a charge generating layer sandwiched between a conductive layer and a charge transport layer as described above or a charge transport layer sandwiched between a conductive layer and a charge generating layer. These structures may be imaged in the conventional xerographic manner which usually includes charging, optical exposure and development.

In one advantageous use of the imaging member of the invention, there is provided an electrophotographic imaging process comprising providing an electrophotographic imaging member comprising a charge generating layer and a charge transport layer, said charge transport layer comprising a π-conjugated polymeric binder and a hole transport compound; depositing a uniform electrostatic charge on said imaging member with a corona charging device; exposing said imaging member to activating radiation in image configuration to form an electrostatic latent image on said imaging member; developing said electrostatic latent image with electrostatically attractable marking particles to form a toner image; transferring said toner image to a receiving member and repeating said depositing, exposing, developing and transferring steps for at least one hour until said corona charging device begins to emit oxides of nitrogen; temporarily stopping said depositing, exposing, developing and transferring steps for at least 10 minutes; and resuming said depositing, exposing, developing and transferring steps.

EXAMPLE 1

Fabrication of the charge transport layers:

The binder polymer and the charge transport molecule were dissolved in a suitable solvent, usually toluene, to approximately 20 weight percent of the solids. A thin film of the polymeric binder and the small active molecule was spread on top of an aluminum plate substrate by spreading the solution using a doctor blade technique. The solvent was allowed to evaporate. The removal of the residual solvent was achieved by heating the specimen at 50°C in a vacuum for 24 hours. The charge carrier mobility was measured by a conventional Time-Of-Flight technique familiar to those skilled in the art, using UV photoexcitation. (Ref. W. E. Spear, J. Non-Cryst. Solids, vol. 1, p. 197 (1969)). The light source was a pulsed (1 ns) nitrogen pump dye laser.

Results:

Using TPD, ETPD or Me-O-TPD as hole transporting molecules, each at 60% wt.% loading, in a binder of PPVP (phenyl substituted PPV where R1 is phenyl and R2 is H), hole drift mobilities near or in excess of 10-3cm2/Vsec were achieved at room temperature and electric fields near the fields typically used in electrophotography. (See the Figure)

EXAMPLE 2

Using the same procedure as in Example 1, but reducing the concentration of the hole transporting molecules from 60 wt% to more preferable levels of 50 wt% (as used in current AMAT P/R) reduced the carrier mobility by a factor of approximately 5, which still achieved the mobilities of the desired levels in excess of 10-5cm2/Vsec, with each of the hole transporting molecules.

EXAMPLE 3

Using the procedure of Example 1, and using TPD as the hole transport molecule in a solid solution in a binder of PPV, where R1 is phenyl, at 60 weight %, hole mobilities of 2x10-4cm2/Vsec, at room temperature and an electric field of E=3x10-5V/cm, were obtained.

COMPARATIVE EXAMPLE 4

Using the procedure of Example 1, and using TPD as the hole transport molecule in a solid solution in polycarbonate as the binder, at 60 weight %, hole mobilities of 3x10-5 cm2/Vsec, at room temperature and an electric field of E=3x10-5V/cm, were obtained.

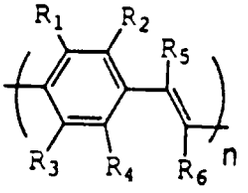
Claims

1. An electrophotographic imaging member comprising a charge generating layer and a charge transport layer, said charge transport layer comprising a nonconductive π-conjugated polymeric binder and at least one charge transport molecule.

2. An electrophotographic imaging member according to claim 1 wherein said π-conjugated polymer is solubilized by at least one substituent.

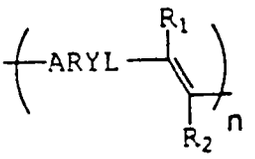
3. An electrophotographic imaging member according to claim 1, wherein said π-conjugated polymer is a substituted poly(phenylene vinylene) of the formula I:

I.



in which:
n is an integer ranging from about 10 to about 10,000; R1, R2, R3, R4, R5 and R6 may each independently represent: hydrogen; an aliphatic group containing from 1 to 16 carbon atoms; an alkoxy group selected from methoxy, ethoxy, propoxy and butoxy; an aromatic group selected from phenyl, mono-, di-, ter-, tetra- and penta- substituted phenyl, wherein each substituent on the aromatic group may be selected from alkyl, p-alkoxy, phenoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl; naphthyl; substituted naphthyl, wherein each substituent on the naphthyl group may be selected from alkyl, p-alkoxy, phenoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl; anthryl; substituted anthryl, wherein each substituent on the anthryl group may be selected from alkyl, p-alkoxy, phenoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl.

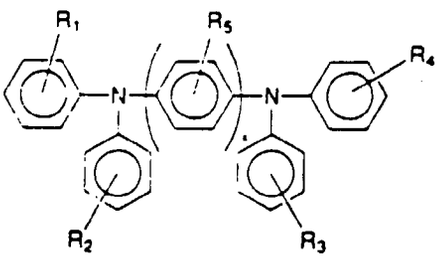
4. An electrophotographic imaging member according to claim 1, wherein said π-conjugated polymer is a substituted poly(arylene vinylene) of the formula II:

II. 

in which:
n is an integer ranging from about 10 to about 10,000; the aryl is derived from an aromatic group selected from naphthalene, anthracene, phenanthrene, fluorene, pyrene, perylene, biphenyl and triphenyl; said aryl may be substituted with one or several aliphatic groups containing from 1 to 16 carbons; an alkoxy group selected from methoxy, ethoxy, propoxy and butoxy; one or several aromatic groups selected from phenyl, mono-, di-, ter-, tetra-, and penta- substituted phenyl, wherein the substituents on the aromatic group may be the same or different and may be selected from alkyl, p-alkoxy, dialkylamino, diarylamino, N-carbazolyl and benzoyl groups; naphthyl; substituted naphthyl, wherein the substituents on the naphthyl group may be selected from alkyl, p-alkoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl groups;
R1 and R2 may be selected from hydrogen; an aliphatic group containing 1 to 16 carbon atoms; an alkoxy group selected from methoxy, ethoxy, propoxy, butoxy and phenoxy; an aromatic groups selected from phenyl, mono-, di-, ter-, tetra-, and penta- substituted phenyl, wherein the substituents on the aromatic group may be selected from alkyl, p-alkoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl groups; naphthyl; substituted naphthyl, wherein the substituents on the naphthyl group may be selected from alkyl, p-alkoxy, dialkylamino, diarylamino, benzoyl and N-carbazolyl groups; naphthoxy; N-carbazolyl; and fluorenyl.

5. An electrophotographic imaging member according to any one of claims 1 to 4 wherein said π-conjugated polymer has charge transporting capability.

6. An electrophotographic imaging member according to claim 1 wherein said charge transport molecule is of the formula:



in which:
n is an integer ranging from 1 to 4; and R1, R2, R3, R4 and R5 may be selected from hydrogen and an aliphatic or an alkoxy group having from 1 to 12 carbon atoms.

7. An electrophotographic imaging member according to claim 1 wherein said charge transport molecule is a hole transport molecule selected from the group consisting of TPD {N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[4,4'-biphe-

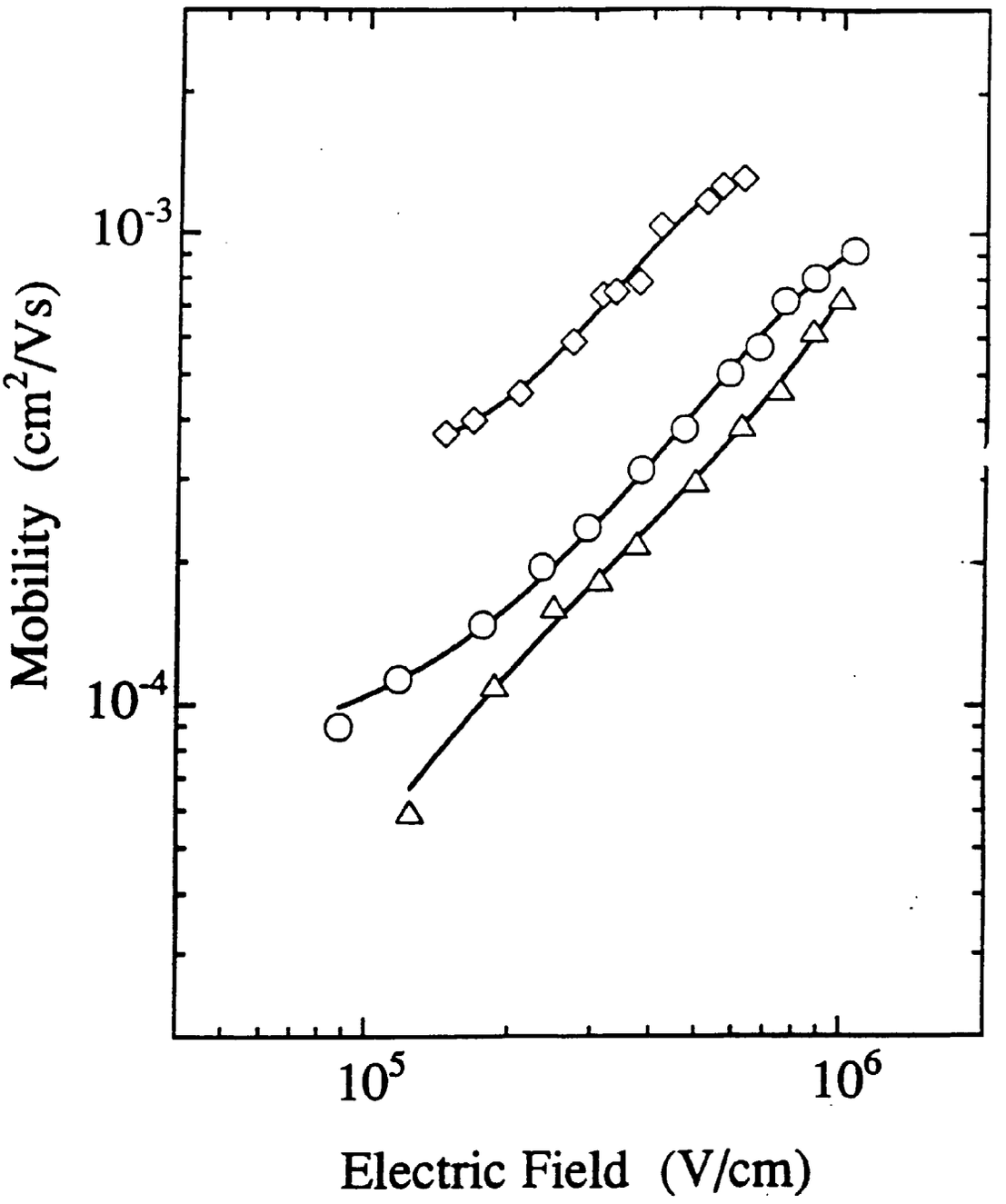
nyl]-1,1'-diamine}, ETPD {N,N'-bis- (3-methylphenyl)-N,N'-bis(4-ethylphenyl)-[4,4'-bis(3,3'-methyl)biphenyl}-1,1'-diamine, e-O-TPD {N,N'-dimethyl-N,N'-bis(3-methoxyphenyl)-[4,4'-biphenyl]-1,1'-diamine} and 1,1'-bis[(di-4-tolylamino)phenyl]cyclohexane.

8. An electrophotographic imaging member according to any one of claims 1 to 7 wherein said charge transport molecule is present in an amount ranging from about 5% to about 60 wt % based on the amount of polymeric binder.

9. An electrophotographic imaging member according to any one of claims 1 to 8 wherein said charge transport layer has a hole mobility of at least 10-5cm2/Vsec.

10. An electrophotographic imaging process comprising

providing an electrophotographic imaging member comprising a charge generating layer and a charge transport layer, said charge transport layer comprising a π-conjugated polymeric binder and a hole transport compound;
depositing a uniform electrostatic charge on said imaging member with a corona charging device;
exposing said imaging member to activating radiation in image configuration to form an electrostatic latent image on said imaging member;
developing said electrostatic latent image with electrostatically attractable marking particles to form a toner image;
transferring said toner image to a receiving member and repeating said depositing, exposing, developing and transferring steps for at least one hour until said corona charging device begins to emit oxides of nitrogen;
temporarily stopping said depositing, exposing, developing and transferring steps for at least 10 minutes; and
resuming said depositing, exposing, developing and transferring steps.


Mobility (cm²/Vs)
10⁻³
10⁻⁴
10⁵
10⁶
Electric Field (V/cm)
60 wt.% ETPD in PPVP
60 wt.% MeO-TPD in PPVP
60 wt.% TPD in PPVP