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(54)Electrophotographic photoconductor for use with liquid toners

(57)A photoconductor for use in electrophotographic reproduction devices is disclosed. This photoconductor exhibits excellent cycling stability and minimized charge transport molecule leaching when used with liquid toners. Further, the photoconductor has a relatively high glass transition temperature. The photoconductors of the present invention utilize, as the binder in the charge transport layer, a specifically defined bisphenol A/bisphenol TMC polycarbonate copolymer which has a bisphenol A: bisphenol TMC weight ratio of from about 30:70 to about 70:30, preferably from about 35:65 to about 65:35, and a polymer molecular weight of from about 10,000 to about 100,000, preferably from about 20,000 to about 50,000.

Description

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TECHNICAL FIELD

The present invention relates to an improved photoconductor, used in electrophotographic reproduction devices particularly in combination with liquid toners, having a charge generating layer and a charge transport layer, which exhibits reduced leaching of the charge transport molecule out of the transport layer, as well as an ability to operate more effectively at higher temperatures.

BACKGROUND OF THE INVENTION

The present invention is a layered electrophotographic photoconductor, i.e., a photoconductor having a metal ground plane member on which a charge generation layer and a charge transport layer are coated, in that order. Although these layers are generally separate, they may be combined into a single layer which provides both charge generation and charge transport functions. Such a photoconductor may optionally include a barrier layer located between the metal ground plane member and the charge generation layer, and/or an adhesion-promoting layer located between the barrier layer (or ground plane member) and the charge generation layer and/or an overcoat layer on the top surface of the charge transport layer.

In electrophotography, a latent image is created on the surface of an insulating, photoconducting material by selectively exposing areas of the surface to light. A difference in electrostatic charge density is created between the areas on the surface exposed and unexposed to the light. The latent electrostatic image is developed into a visible image by electrostatic toners containing pigment components and thermoplastic components. The toners, which may be liquids or powders, are selectively attracted to the photoconductor surface either exposed or unexposed to light, depending on the relative electrostatic charges on the photoconductor surface, development electrode and the toner. The photoconductor may be either positively or negatively charged, and the toner system similarly may contain negatively or positively charged particles.

A sheet of paper or intermediate transfer medium is given an electrostatic charge opposite that of the toner and then passed close to the photoconductor surface, pulling the toner from the photoconductor surface onto the paper or intermediate medium still in the pattern of the image developed from the photoconductor surface. A set of fuser rollers melts and fixes the toner in the paper, subsequent to direct transfer, or indirect transfer when an intermediate transfer medium is used, producing the printed image.

The electrostatic printing process, therefore, comprises an ongoing series of steps wherein the photoconductor surface is charged and discharged as the printing takes place. It is important to keep the charge voltage and discharge voltage on the surface of the photoconductor constant as different pages are printed to make sure that the quality of the images produced is uniform (cycling stability). If the charge/discharge voltage is changed each time the drum is cycled, e.g., if there is fatigue or other significant change in the photoconductor surface, the quality of the pages printed will not be uniform and will be unsatisfactory.

It is desirable to use liquid toners in the electrophotographic printing process in order to get the highest possible resolution on the printed page. However, on most photoconductor surfaces, the charge transport molecules present on the photoconductor drum tend to leach into the oil carrier present in the toner. This results in higher (i.e., non-uniform) discharge voltages on the photoconductor surface and, therefore, poor quality in the printed pages produced. Severe penetration of the oil through the transport layer may also disrupt the performance of the charge generation layer. In some embodiments of a liquid toner printing process, higher fusing temperatures are required, leading to temperatures at the photoconductor surface that may approach the glass transition temperature (Tg) of the transport formulation. Unless the glass transition temperature of the photoconductor surface is high enough, these operating temperatures can cause softening of the photoconductor surface, and negatively affect the quality of the electrophotographic images produced.

Thus, it is important, when designing a photoconductor used with liquid toners, to have one which minimizes charge transport molecule leaching and has a relatively high glass transition temperature, while maximizing the cycling stability of the electrophotographic surface.

It has now been found that the use of specific binders in the charge transport layer of an organic photoconductor provides reduced leaching of the charge transport component into the toner, as well as a relatively high glass transition temperature for the transport layer, while maintaining electrostatic performance and even improving print resolution. Further, the decreased leaching permits the use of higher levels of charge transport molecule in the transport layer which results in better electrical properties. The binders which exhibit these unexpected properties are copolymers of bisphenol A and bisphenol TMC (TMC = 3,3,5-trimethylcyclohexylidene diphenol) formulated within specific relative monomer ratios and polymer molecular weight ranges.

U.S. Patent 5,382,489, Ojima, et al., issued January 17, 1995 and filed July 30, 1993, describes an electrophotographic photoreceptor which has enhanced abrasion resistance and a reduced tendency to toner filming. This photore-

ceptor utilizes a binder containing a mixture of specific polycarbonate resins. 3,3,5-trimethylcyclohexylidene diphenol is not one of the monomers included in the specifically described copolymer resins. Further, there is no suggestion of minimized transport molecule leaching or high glass transition temperatures for the disclosed photoreceptors.

United Kingdom Patent Application 2,269,677A, Vollmer, et al., published February 16, 1994, describes a layered organic photoconductor containing a dye dispersed in an aromatic ester polycarbonate in the charge generating layer and a charge transport molecule dispersed in a polycarbonate binder in the charge transport layer. The binder used in the charge transport layer is bisphenol A. It is taught that this electrophotographic surface can be used with liquid toner and demonstrates leaching benefits for the charge transport molecule. No copolymers of bisphenol A and bisphenol TMC are described.

U.S. Patent 5, 130,215, Adley, et al., issued July 14, 1992, describes layered electrophotographic photoconductors utilizing specifically defined ordered copolyestercarbonate binders in the charge generating and/or charge transport layers. These binders are taught to minimize changes in the charge and discharge voltages over the lifetime of the photoconductive surface, with reduced discharge voltage fatigue. Copolymers of bisphenol A and bisphenol TMC are not described.

U.S. Patent 5,190,817, Terrell, et al., issued March 2, 1993, describes photoconductive recording materials utilizing, as a binder, a polyestercarbonate polymer containing 10 to 48 mole percent aromatic carbonate units and 52-90 mole percent aromatic polyester units. These structures are taught to provide good abrasion resistance and high photosensitivity. Specific exemplified copolymers include bisphenol A units, but no bisphenol A/bisphenol TMC copolymers are described or suggested.

Research Disclosures, <u>338</u>:451 (1992), discloses the use of bisphenol TMC as a binder in the charge generating or charge transport layer of an organic photoconductor. Bisphenol A/bisphenol TMC copolymers are taught to have good heat stability, high glass transition temperatures, high impact strength, good transparency, and good solubility in a variety of solvents. These binders are not disclosed for use with liquid toners, nor is the minimization of charge transport molecule leaching (a benefit specifically related to liquid toner usage) taught.

As can be seen, none of these publications and patents disclose photoconductor surfaces which utilize the specific bisphenol A/bisphenol TMC copolymers described in the present application in conjunction with a liquid toner to achieve the benefits of the present invention. Further, there is no suggestion that the bisphenol A/bisphenol TMC binders provide such benefits when compared to bisphenol A binders.

SUMMARY OF THE INVENTION

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The present invention relates to a photoconductive member for use with a liquid toner which includes a charge transport layer comprising an effective amount of a charge transport molecule (preferably a hydrazone, such as DEH) and an effective amount of a binder resin which is a copolymer of bisphenol A and bisphenol TMC, preferably having a bisphenol A: bisphenol TMC monomer weight ratio of from about 40:60 to about 60:40 and a polymer molecular weight of from about 20,000 to about 50,000.

More specifically, the present invention relates to a photoconductive member for use with a liquid toner comprising:

- (a) a ground plane member;
- (b) a charge generating layer carried by said ground plane member comprising an effective amount of a photosensitive dye dispersed in a binder; and
- (c) a charge transport layer carried by said charge generating layer comprising from about 30 parts to about 70 parts by weight of a charge transport molecule (preferably a hydrazone, such as DEH) and from about 30 parts to about 70 parts by weight of a binder resin which is a copolymer of bisphenol A and bisphenol TMC, wherein the bisphenol A: bisphenol TMC weight ratio is from about 35:65 to about 65:35 (preferably from about 40:60 to about 60:40), and the polymer has a molecular weight of from about 10,000 to about 100,000 (preferably from about 20,000 to about 50,000).

As used herein, all percentages, ratios and parts are "by weight" unless otherwise specified.

DETAILED DESCRIPTION OF THE INVENTION

Photoconductors of the present invention find utility in electrophotographic reproduction devices, such as copiers and printers, and may be generally characterized as layered photoconductors wherein one layer (the charge generating layer) absorbs light and, as a result, generates electrical charge carriers, while the second layer (the charge transport layer) transports those charge carriers to the exposed surface of the photoconductor.

While these devices frequently have separate charge generation and charge transport layers, with the charge transport layer being overlaid on the charge generating layer, it is also possible to combine the charge generating and charge transport functions into a single layer in the photoconductor.

In the photoconductor structure, a substrate, which may be flexible (such as a flexible web or a belt) or inflexible (such as a drum), is uniformly coated with a thin layer of metallic aluminum. The aluminum layer functions as an electrical ground plane. In a preferred embodiment, the aluminum is anodized, which turns the aluminum surface into a thicker aluminum oxide surface (having a thickness of from about 2 to about 12 microns, preferably from about 4 to about 7 microns). The ground plane member may be a metallic plate (made, for example, from aluminum or nickel), a metallic drum or foil, a plastic film on which is vacuum evaporated aluminum, tin oxide, or indium oxide, for example, or a conductive substance-coated paper or plastic film or drum.

The aluminum layer is then coated with a thin, uniform thickness charge generating layer comprising a photosensitive dye material dispersed in a binder. Finally, the uniform thickness charge transport layer is coated onto the charge generating layer. The charge transport layer comprises a specifically defined bisphenol A/bisphenol TMC copolymer binder containing a charge transport molecule.

In the case of a single layer structure, a photosensitive layer comprises a charge generating material, a charge transport material, and a binder resin (i.e., a bisphenol A/bisphenol TMC copolymer binder resin).

The thickness of the various layers in the structure is important and is well known to those skilled in the art. In an exemplary photoconductor, the ground plane layer has a thickness of from about 0.01 to about 0.07 microns, the charge generating layer has a thickness of from about 0.05 to about 5.0 microns, preferably from about 0.1 to about 2.0 microns, most preferably from about 0.1 to about 0.5 micron, and the charge transport layer has a thickness of from about 10 to about 25 microns, preferably from about 20 to about 25 microns. If a barrier layer is used between the ground plane and the charge generating layer, it has a thickness of from about 0.05 to about 2.0 microns. Where a single charge generating/charge transport layer is used, that layer generally has a thickness of from about 10 to about 25 microns.

In forming the charge generating layer utilized in the present invention, a fine dispersion of a small particle photosensitive dye material is formed in a binder material, and this dispersion is coated onto the ground plane layer. This is generally done by preparing a dispersion containing the photosensitive dye, the binder and a solvent, coating the dispersion onto the ground plane member, and drying the coating.

Any organic photosensitive dye material known in the art to be useful in photoconductors may be used in the present invention. Examples of such materials belong to one of the following classes:

- (a) polynuclear quinones, e.g., anthanthrones
- 30 (b) quinacridones

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- (c) naphthalene 1,4,5,8- tetracarboxylic acid derived pigments, such as perinones,
- (d) phthalocyanines and naphthalocyanines, e.g., H₂ phthalocyanine in X crystal form (see, for example, U.S. Patent 3,357,989), metal phthalocyanines and naphthalocyanines (including those having additional groups bonded to the central metal)
- (e) indigo- and thioindigo dyes
- (f) benzothioxanthene derivatives
- (g) perylene 3,4,9,10-tetracarboxylic acid derived pigments, including condensation products with amines (perylene diimides) and o-diamines (perylene bisimidazoles)
- (h) polyazo-pigments, including bisazo-, trisazo-, and tetrakisazo- pigments
- 40 (i) squarylium dyes
 - (j) polymethine dyes
 - (k) dyes containing quinazoline groups (see, for example UK 1,416,602)
 - (I) triarylmethane dyes
 - (m) dyes containing 1,5 diamino anthraquinone groups
- 45 (n) thiapyrylium salts
 - (o) azulenium salts; and
 - (p) pyrrolo-pyrrole pigments.

Such materials are described in greater detail in U.S. Patent 5,190,817, Terrell, et al., issued March 2, 1993, incorporated herein by reference.

Preferred photosensitive dyes for use in the present invention are phthalocyanine dyes which are well known to those skilled in the art. Examples of such materials are taught in U.S. Patent 3,816,118, Byrne, issued June 11, 1974, incorporated herein by reference. Any suitable phthalocyanine may be used to prepare the charge generating layer portion of the present invention. The phthalocyanine used may be in any suitable crystalline form. It may be unsubstituted or substituted either (or both) in the six-membered aromatic rings and at the nitrogens of the five-membered rings. Useful materials are described, and their synthesis given, in Moser and Thomas, *Phthalocyanine Compounds*, Reinhold Publishing Company, 1963, incorporated herein by reference. Particularly preferred phthalocyanine materials are those in which the metal central in the structure is titanium (i.e., titanyl phthalocyanines) and metal-free phthalocyanines. The metal-free phthalocyanines are also particularly preferred, especially the X-crystalline form metal-free phthalocyanines.

Such materials are disclosed in U.S. Patent 3,357,989, Byrne, et al., issued December 12, 1967; U.S. Patent 3,816,118, Byrne, issued June 11, 1974, and U.S. Patent 5,204,200, Kobata, et al., issued April 20, 1993, all of which are incorporated herein by reference. The X-type non-metal phthalocyanine is represented by the formula:

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Such materials are available in an electrophotographic grade of very high purity, for example, under the trade name Progen-XPC from Zeneca Colours Company.

As the binder, a high molecular weight polymer having hydrophobic properties and good forming properties for an electrically insulating film is preferably used. These high molecular weight polymers include, for example, the following materials, but are not limited thereto: polycarbonates, polyesters, methacrylic resins, acrylic resins, polyvinyl chlorides, polyvinylidene chlorides, polystyrenes, polyvinylbutyrals, ester-carbonate copolymers, polyvinyl acetates, styrene-butadiene copolymers, vinylidene chloride - acrylonitrile copolymers, vinyl chloride-vinyl acetate copolymers, vinyl chloride-vinyl acetate copolymers, styrene-alkyd resins, and poly-N-vinylcarbazoles. These binders can be used in the form of a single resin or in a mixture of two or more resins.

Preferred binder materials include the bisphenol A/bisphenol TMC copolymers described below, medium molecular weight polyvinyl chlorides, polyvinylburyrals, ester-carbonate copolymers, and mixtures thereof. The polyvinyl chloride compounds useful as binders have an average molecular weight (weight average) of from about 25,000 to about 300,000, preferably from about 50,000 to about 125,000, most preferably about 80,000. The PVC material may contain a variety of substituents including chlorine, oxirane, acrylonitrile or butyral, although the preferred material is unsubstituted. Polyvinyl chloride materials useful in the present invention are well known to those skilled in the art. Examples of such materials are commercially available as GEON 110X426 from the Geon Company. Similar polyvinyl chlorides are also available from the Union Carbide Corporation.

In forming the charge generating layer, a mixture of the photosensitive dye is formed in the binder material. The amount of photosensitive dye used is that amount which is effective to provide the charge generation function in the photoconductor. This mixture generally contains from about 10 parts to about 50 parts, preferably from about 10 parts to about 30 parts, most preferably about 20 parts of the photosensitive dye component and from about 50 parts to about 90 parts, preferably from about 70 parts to about 90 parts, most preferably about 80 parts of the binder component.

The photosensitive dye/binder mixture is then mixed with a solvent or dispersing medium for further processing. The solvent selected should: (1) be a true solvent for high molecular weight polymers, (2) be non-reactive with all components, and (3) have low toxicity. Examples of dispersing media/solvents which may be utilized in the present invention, used either alone or in combination with preferred solvents, include hydrocarbons, such as hexane, benzene, toluene and xylene; halogenated hydrocarbons, such as methylene chloride, methylene bromide, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,1-trichloroethane, 1,2-dichloropropane, chloroform, bromoform, and chlorobenzene; ketones, such as acetone, methylethyl ketone and cyclohexanone; esters, such as ethyl acetate and butyl acetate; alcohols, such as methanol, ethanol, propanol, butanol, cyclohexanol, heptanol, ethylene glycol, methyl cellosolve, ethyl cellosolve and cellosolve acetate, and derivatives thereof; ethers and acetals, such as tetrahydrofuran, 1,4-dioxane, furan and furfural; amines, such as pyridine, butylamine, diethylamine, ethylenediamine and isopropanol amine; nitrogen compounds including amides, such as N,N-dimethylformamide; fatty acids and phenols; and sulphur and phosphorus compounds, such as carbon disulfide and triethyl phosphate. The preferred solvents for use in the present invention are

methylene chloride, cyclohexanone and tetrahydrofuran (THF). The mixtures formed include from about 1% to about 50%, preferably from about 2% to about 10%, most preferably about 5% of the photosensitive dye/binder mixture and from about 50% to about 99%, preferably from about 90% to about 98%, most preferably about 95% of the solvent/dispersing medium.

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The entire mixture is then ground, using a conventional grinding mechanism, until the desired dye particle size is reached and is dispersed in the mixture. The organic pigment may be pulverized into fine particles using, for example, a ball mill, homogenizer, paint shaker, sand mill, ultrasonic disperser, attritor or sand grinder. The preferred device is a sand mill grinder. The photosensitive dye has a particle size (after grinding) ranging from submicron (e.g., about 0.01 micron) to about 5 microns, with a particle size of from about 0.05 to about 0.5 micron being preferred. The mixture may then be "let down" or diluted with additional solvent to about 2-5% solids, providing a viscosity appropriate for coating, for example, by dip coating.

The charge generating layer is then coated onto the ground plane member. The dispersion from which the charge generating layer is formed is coated onto the ground plane layer using methods well known in the art including dip coating, spray coating, blade coating or roll coating, and is then dried. The preferred method for use in the present invention is dip coating. The thickness of the charge generating layer formed should preferably be from about 0.1 to about 2.0 microns, most preferably around 0.5 micron. The thickness of the layer formed will depend upon the percent solids of the dispersion into which the ground plane member is dipped as well as the time and temperature of the dip process. Once the ground plane member has been coated with the charge generating layer, it is allowed to dryg for from about 10 to about 100 minutes, preferably from about 30 to about 60 minutes, at a temperature of from about 60°C to about 160°C, preferably about 100°C.

The charge transport layer is then prepared and coated on the ground plane member so as to cover the charge generating layer. The charge transport layer is formed from a solution containing a charge transport molecule in a bisphenol A/bisphenol TMC copolymer binder, coating this solution onto the charge generating layer and drying the coating.

In principle, a large class of known hole or electron transport molecules may be used in the present invention. Examples of such compounds include poly-N-vinylcarbazoles and derivatives, poly- τ - carbazolyl-glutamate and derivatives, pyreneformaldehyde condensates and derivatives, polyvinylpyrene, polyvinylphenanthrene, oxazole derivatives, oxadiazole derivatives, imidazole derivatives, 9-(p-diethylaminostyryl) anthracene, 1,1-bis (4-dibenzylaminophenyl) propane, styrylanthracene, styrylpyrazoline, arylamines, aryl-substituted butadienes, phenylhydrazones and α -stilbene derivatives.

These charge transport molecules or systems of molecules are well known in the art. A fundamental requirement of these low molecule weight organic compounds is that mobility (positive hole transfer through the layer) must be such that charge can transit the layer in a time that is short compared to the time between exposure and image development. Hole transport occurs through the transfer of charge from states associated with the donor/acceptor functionalities. This can be described as a one-electron oxidation-reduction or donor-acceptor process. Oxidation potential measurements, as well as charge mobility measurements, have been used to evaluate the efficacy of charge transport molecules. Examples of such compounds are disclosed in U.S. Patent 5,053,303, Sakaguchi, et al., issued October 1, 1991, incorporated herein by reference. Preferred charge transport molecules are selected from hydrazones, butadienes, pyrazolines, and mixtures of those compounds. Hydrazones useful in the present invention are those compounds having the following general formula:

$$R^3$$
 R^4
 R^1
 $CH=N-N$
 R^8

wherein R¹, R⁸ and R⁹, independently from each other, represent a hydrogen or a lower alkyl, and R³ and R⁴, independently from each other, represent a lower alkyl or aryl.

Butadienes useful in the present invention are those compounds having the following general formula:

$$C = CH - CH = C$$

$$R^{7}$$

$$R^{5}$$

$$R^{6}$$

$$R^{3}$$

$$R^{1}$$

wherein R^3 and R^4 , independently from each other, represent a lower alkyl, and R^1 , R^5 , R^6 , R^{10} and R^{11} , independently from each other, represent hydrogen or a lower alkyl.

The pyrazoline compounds useful in the present invention are those having the following structural formula:

wherein R^3 , R^4 , R^{12} and R^{13} , independently from each other, represent a lower alkyl, and R^{14} represents a phenyl group which may contain one or more substituents.

Hydrazones are the preferred charge transport molecules for use in the present invention. The most preferred charge transport molecule is known as DEH, having the chemical name p-diethylaminobenzaldehyde-N,N-diphenylhydrazone. This compound has the following structural formula:

The binder used in the charge transport layer of the present invention is a copolymer of bisphenol A and bisphenol TMC. This copolymer has the following structural formula:

wherein a and b are such that the weight ratio of bisphenol A to bisphenol TMC is from about 30:70 to about 70:30, preferably from about 35:65 to about 65:35, most preferably from about 40:60 to about 60:40. The molecular weight (weight average) of the polymer is from about 10,000 to about 100,000, preferably from about 20,000 to about 50,000, most preferably from about 30,000 to about 40,000.

Bisphenol A polycarbonate (isopropylidene diphenol polycarbonate) has the following structural formula:

$$\begin{array}{c|c}
\hline
 & CH_3 & O \\
\hline
 & CH_3 & O \\
\hline
 & CH_3 & O \\
\hline
 & D & D
\end{array}$$

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Bisphenol TMC polycarbonate (3,3,5-trimethyl-cyclohexylidene diphenol polycarbonate) has the following struc-30 tural formula:

These materials are commercially available from Miles, Inc., under the tradenames APEC DP9-9202 (A:TMC weight ratio = about 57:43, molecular weight = about 35,000) and APEC DP9-9203 (A:TMC weight ratio = about 36:64, molecular weight = about 35,000).

Typical industrial preparation of polycarbonates is accomplished by the reaction of a diphenol with phosgene, COCl₂. The bisphenol A/bisphenol TMC polycarbonate resins utilized as binders in the present invention can be prepared using the following general reaction scheme:

The charge transport layer may also contain certain optional components which are well known in the art, used at their art established levels. Examples of such components include silicone additives to improve the flow of the layer as it coats the photoconductor surface (e.g., low molecular weight polydimethylsiloxane materials), and room light protectors (such as Acetosol yellow dye). In addition to the bisphenol A/bisphenol TMC copolymers, other known binders may

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be included in minor amounts.

The mixture of charge transport molecule(s) and binder, having a composition of from about 30% to about 70%, preferably from about 30% to about 50%, most preferably about 35% to about 45% of the charge transport molecule(s) and from about 30% to about 70%, preferably from about 50% to about 70%, most preferably from about 55% to about 65% of the binder, is then formulated. The amount of charge transport molecule utilized is that amount which is effective to perform the charge transport function in the photoconductor. The binders used both in the charge transport and charge generating layers are used in an amount effective to perform their binder function. This mixture is added to a solvent, such as those discussed above for use in forming the charge generation layer. Preferred solvents are THF, cyclohexanone and methylene chloride. It is preferred that the solution contain from about 10% to about 40%, preferably about 25% of the binder/transport molecule mixture and from about 60% to about 90%, preferably about 75% of the solvent. The charge transport layer is then coated onto the charge generating layer and the ground plane member using any of the conventional coating techniques discussed above. Dip coating is preferred. The thickness of the charge transport layer is generally from about 10 to about 25 microns, preferably from about 20 to about 25 microns. The percentage solids in the solution, viscosity, the temperature of the solution, and the withdrawal speed control the thickness of the transport layer. The layer is usually heat dried for from about 10 to about 100 minutes, preferably about 30 to about 60 minutes at a temperature of from about 60°C to about 160°C, preferably about 100°C. Once the transport layer is formed on the electrophotographic member, post-treatment of the layer by either UV curing or thermal annealing is preferred in that it further reduces the rate of transport molecule leaching, especially at higher transport molecule concentrations.

In addition to the layers discussed above, an undercoat layer may be placed between the ground plane member (substrate) and the charge generating layer. This is essentially a primer layer which covers over any imperfections in the substrate layer and improves the uniformity of the thin charge generation layer formed. Materials which may be used to form this undercoat layer include epoxy, polyamide and polyurethane. It is also possible to place an overcoat layer (i.e., a surface protecting layer) on top of the charge transport layer. This protects the charge transport layer from wear and abrasion during the printing process. Materials which may be used to form this overcoat layer include polyurethane, phenolic, polyamide and epoxy resins. These structures are well known to those skilled in the art.

The following example illustrates the photoconductors of the present invention. This example is intended to be illustrative and not limiting of the present invention.

EXAMPLE

A two layer photoconductor drum of the present invention is made in the following manner.

A representative charge generating layer formulation is prepared as follows: 8.99g medium molecular weight polyvinyl chloride (Geon 110X426, available from Geon Company) is dissolved in 213.56g THF. 2.25g X-form H_2 (pc) ["metal free" phthalocyanine, Zeneca Colours] is added to this solution along with 2 mm glass beads, and milled for 24 hours on a Red Devil paint shaker. After the initial milling, 126.44g additional THF is added to let down the formulation, followed by milling for an additional 30 minutes. This formulation is coated onto a 40 mm anodized aluminum core to produce the charge generating layer. When the coat speed is 1.2 feet/minute, the optical density of the layer is about 1.39 (optical densities measured with a Macbeth TR524 densitometer); when the coat speed is 2.7 feet/minute, the optical density of the layer is about 1.77. The coating thickness of the charge generating layer can also be measured by weight. Following coating of the formulation, the charge generating layer is dried for 1 hour at 100°C.

A representative charge transport formulation is prepared as follows: 36.55g Apec DP9-9203 polycarbonate resin and 3.33g Vitel 2200 polyester (commercially available from Goodyear Chemicals) are added by portions to 250 ml THF with stirring until the polymers are completely dissolved. Then, 26.95g DEH (hole transport material, commercially available from Eastman Chemical), 0.488 Acetosol 5 GLS (room light absorber, commercially available from Sandoz Chemical), and 2.5 drops DC-200 silicone oil (surfactant, commercially available from Dow Corning) are added to the solution. The resulting transport formulation is coated on top of the charge generating layer by dip coating. When a coating speed of 1.5 feet/minute is used, a coating thickness between about 15 and 18 microns is obtained. After coating, the transport layer is dried for one hour at 100°C.

When used with a liquid toner, the formulated photoconductor exhibits excellent and superior cycling stability and minimal leaching of the DEH transport molecule, in comparison with photoconductors utilizing transport layer binder resins composed solely of bisphenol-A polycarbonates. The electrophotoconductive member produced also has a relatively high glass transition temperature.

Claims

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- A photoconductive member for use with a liquid toner which includes a charge transport layer comprising an effective amount of a charge transport molecule and an effective amount of a binder resin which is a copolymer of bisphenol A and bisphenol TMC.
- 2. A photoconductive member according to Claim 1 having a charge transport layer which contains from about 30% to about 70% of the charge transport molecule and from about 30% to about 70% of the binder resin.
- 35 3. A photoconductive member according to Claim 2 wherein the charge transport molecule is selected from the group consisting of butadienes, hydrazones, pyrazolines, and mixtures thereof.
 - 4. A photoconductive member according to Claim 3 wherein the binder resin has a bisphenol A: bisphenol TMC weight ratio of from about 30:70 to about 70:30 and a polymer molecular weight from about 10,000 to about 100,000.
 - **5.** A photoconductive member according to Claim 4 wherein the charge transport layer comprises from about 30% to about 50% of the charge transport molecule and from about 50% to about 70% of the binder resin.
- 45 **6.** A photoconductive member according to Claim 5 wherein the charge transport molecule is selected from hydrazones.
 - 7. A photoconductive member according to Claim 5 wherein the binder resin has a bisphenol A:bisphenol TMC weight ratio of from about 35:65 to about 65:35 and a polymer molecular weight of from about 20,000 to about 50,000.
 - 8. A photoconductive member according to Claim 7 wherein the binder resin has a bisphenol A:bisphenol TMC weight ratio of from about 40:60 to about 60:40.
- **9.** A photoconductive member according to Claim 8 wherein the binder resin has a polymer molecular weight of from about 30,000 to about 40,000.
 - 10. A photoconductive member according to Claim 6 wherein the charge transport molecule is DEH.
 - 11. A photoconductive member according to Claim 10 wherein the charge transport layer comprises from about 35%

to about 45% of the charge transport molecule and from about 55% to 65% of the binder resin.

- **12.** A photoconductive member according to Claim 11 wherein the binder resin has a bisphenol A: bisphenol TMC weight ratio of from about 40:60 to about 60:40.
- **13.** A photoconductive member according to Claim 12 wherein the binder resin has a polymer molecular weight of from about 20,000 to about 50,000.
- **14.** A photoconductive member according to Claim 13 wherein the binder resin has a polymer molecular weight of from about 30,000 to about 40,000.
 - **15.** A photoconductive member according to Claim 4 wherein the charge transport layer has a thickness of from about 10 microns to about 25 microns.
- 15 **16.** The photoconductive member of Claim 4 in combination with a liquid toner.
 - 17. The photoconductive member of Claim 14 in combination with a liquid toner.
 - **18.** A photoconductive member for use with a liquid toner comprising:

(a) a ground plane member;

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- (b) a charge generating layer carried by said ground plane member comprising an effective amount of a photosensitive dye dispersed in a binder; and
- (c) a charge transfer layer carried by said charge generating layer comprising from about 30% to about 70% by weight of a charge transport molecule and from about 30% to about 70% by weight of a binder resin which is a copolymer of bisphenol A and bisphenol TMC, wherein the bisphenol A:bisphenol TMC weight ratio is from about 35:65 to about 65:35, and the polymer has a molecular weight of from about 10,000 to about 100,000.
- 19. The photoconductive member according to Claim 18 wherein the charge transport layer comprises from about 30% to about 50% of the charge transport molecule and from about 50% to about 70% of the binder resin, the charge transport molecule is DEH, and in the binder resin the bisphenol A: bisphenol TMC weight ratio is from about 40:60 to about 60:40 and the polymer molecular weight is from about 20,000 to about 50,000.
- 20. The photoconductive member according to Claim 19 in combination with a liquid toner.



EUROPEAN SEARCH REPORT

Application Number EP 96 30 6948

Category	Citation of document with indication, wher of relevant passages	e appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Х	WO-A-93 24861 (AGFA-GEVAERT) * page 12, last paragraph; c * page 14; example B6 * * page 15, paragraph 2 * * page 18, line 26 - line 27	claim 1 *	1-20	G03G5/05
A,D	GB-A-2 269 677 (LEXMARK) * page 1, line 31 - page 2, 1 *	line 14; clai	m	
A	US-A-4 081 274 (A.M.HORGAN)		4,7,9, 13,14, 18,19	
	* claims 1-7 *		10,19	
				TECHNICAL FIELDS SEARCHED (Int.Cl.6)
				G03G
	The present search report has been drawn up f	or all claims		
	Place of search Date	of completion of the search		Examiner
	THE HAGUE 27	November 199	6 Var	nhecke, H
X : par Y : par doc	CATEGORY OF CITED DOCUMENTS ticularly relevant if taken alone ticularly relevant if combined with another ument of the same category mological backgroundwritten disclosure	E : earlier pacent after the filin D : document cite L : document cite	ciple underlying th document, but pub g date d in the application d for other reasons	e invention lished on, or