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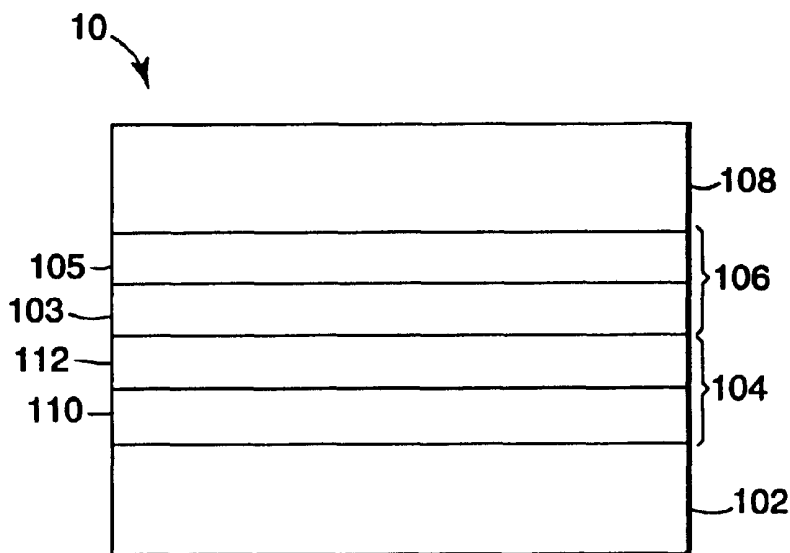
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(54) Title: ORGANIC PHOTORECEPTORS FOR LIQUID ELECTROPHOTOGRAPHY



(57) Abstract: An organic photoreceptor ("OPR") including a barrier layer including an undercoat formed from a composition including a poly(vinyl alcohol), a methylvinyl ether/maleic anhydride copolymer, and a crosslinker and an overcoat formed from a composition including a material selected from the group consisting of an amine-containing hydroxyether, an amide-containing hydroxyether, and a combination thereof, provides sufficient protection to the organic photoreceptor from damage due to corona-induced charge injection; is substantially inert with respect to the organic photoconductive layer; exhibits sufficient resiliency to withstand shear, compressional and tensional forces exerted on the belt as it passes through an electrophotographic system when the photoreceptor is used in an endless belt form; and provides sufficient protection to limit or prevent a liquid toner from contacting the organic photoconductor that may result in crazing and/or cracking of the organic photoreceptor during use.



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ORGANIC PHOTORECEPTORS FOR LIQUID ELECTROPHOTOGRAPHY

Background of the Invention

5 This invention relates to organic photoreceptors suitable for use in electrophotography and, in particular, in liquid electrophotography.

 In electrophotography, a photoreceptor in the form of a plate, belt, or drum having an electrically insulating photoconductive element on an electrically conductive substrate is imaged by first uniformly electrostatically charging the
10 surface of the photoconductive layer, and then exposing the charged surface to a pattern of light. The light exposure selectively dissipates the charge in the illuminated areas, thereby forming a pattern of charged and uncharged areas. A liquid or solid toner is then deposited in either the charged or uncharged areas to create a toned image on the surface of the photoconductive layer. The resulting
15 visible toner image can be transferred to a suitable receiving surface such as paper. The imaging process can be repeated many times.

 Both single layer and multilayer photoconductive elements have been used. In the single layer embodiment, a charge transport material and charge generating material are combined with a polymeric binder and then deposited on the electrically
20 conductive substrate. In the multilayer embodiment, the charge transport material and charge generating material are in the form of separate layers, each of which can optionally be combined with a polymeric binder, deposited on the electrically conductive substrate. Two arrangements are possible. In one arrangement (the “dual layer” arrangement), the charge generating layer is deposited on the electrically
25 conductive substrate and the charge transport layer is deposited on top of the charge generating layer. In an alternate arrangement (the “inverted dual layer” arrangement), the order of the charge transport layer and charge generating layer is reversed.

 In both the single and multilayer photoconductive elements, the purpose of
30 the charge generating material is to generate charge carriers (i.e., electron-hole pairs) upon exposure to light. The purpose of the charge transport material is to accept one

of these charge carriers and transport them through the charge transport layer in order to discharge a surface charge on the photoconductive element.

To produce high quality images, particularly after multiple cycles, it is desirable for the charge transport material to form a homogeneous solution with the polymeric binder and remain in solution. In addition, it is desirable to maximize the amount of charge which the charge transport material can accept (indicated by a parameter known as the acceptance voltage or " V_{acc} "), and to minimize retention of that charge upon discharge (indicated by a parameter known as the residual voltage or " V_{res} ").

Liquid toners generally produce superior images compared to dry toners. However, liquid toners also can facilitate stress crazing in the photoconductive element. Stress crazing, in turn, leads to printing defects such as increased background. It also degrades the photoreceptor, thereby shortening its useful lifetime. The problem is particularly acute when the photoreceptor is in the form of a flexible belt included in a compact imaging machine that employs small diameter support rollers (e.g., having diameters no greater than about 40 mm) confined within a small space. Such an arrangement places significant mechanical stress on the photoreceptor, and can lead to degradation and low quality images.

One solution developed has been to provide a barrier layer to an organic photoreceptor. Conventional barrier layers have been formed from a variety of materials, examples of which include crosslinkable siloxanol-colloidal silica hybrids (as disclosed, e.g., in U.S. Patent Nos. 4,439,509; 4,606,934; 4,595,602; and 4,923,775); a coating formed from a dispersion of hydroxylated silsesquioxane and colloidal silica in an alcohol medium (as disclosed, e.g., in U.S. Patent No. 4,565,760); a polymer resulting from a mixture of polyvinyl alcohol with methyl vinyl ether/maleic anhydride copolymer (e.g., in U.S. Patent No. 5,124,220); a coating formed from an organic polymer (such as polyacrylates, polyurethanes, polyvinyl acetals, sulfonated polyesters, and mixtures of polyvinyl alcohol with methylvinylether/maleic anhydride copolymer) and silica (e.g., in International Publication No. WO 95/02853); and polyvinyl butyral crosslinked with

methylvinylether/maleic anhydride copolymer, such as that commercially available under the trade designation GANTREZ AN 169, from ISP, Wayne, NJ.

5 However, it has been found that these barrier layers do not provide an organic photoconductive layer with adequate protection from liquid contact when a liquid toner is utilized. Furthermore, it has been found that these barrier layers do not possess sufficient resiliency to be used in belt form, as evidenced by stress fractures that developed in the charge transport layers when subjected to stress testing in the presence of a liquid toner.

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Summary of the Invention

Thus, what is yet needed is an organic photoreceptor including a barrier layer that possesses improved resistance to liquid toners, even in relative high humidity (i.e., relative humidity above about 65%) while maintaining other suitable electrophotographic properties, such as stability under charge-discharge cycling. It is also highly desirable that such a barrier layer possesses sufficient resiliency so that the organic photoreceptor is useful in belt form.

15 Accordingly, one aspect of the present invention provides an organic photoreceptor that includes an organic photoconductor having a first major surface and a second major surface; a barrier layer on the first major surface of the photoconductor formed from a barrier layer coating comprising an undercoat and an overcoat thereon. The photoreceptor also includes a release layer.

25 Another aspect of the present invention provides an electrophotographic system for producing a multi-colored image. The system includes a photoreceptor, as described above; a positioner for movably positioning the photoreceptor in order that a given portion of the photoreceptor sequentially advances through a plurality of locations in a single pass; an eraser for erasing any previously accumulated charge from the photoreceptor; a charger for charging the photoreceptor to a predetermined charge level; at least one image-wise exposing device for exposing the photoreceptor with radiation modulated in accordance with an image data for one of a plurality of colors in order to partially discharge the photoreceptor to a first discharge level to produce an image-wise distribution of charges on the photoreceptor corresponding to

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the image data for the one of a plurality of colors; at least one applicator to apply a first color liquid toner comprising charged particles of the first color and transparent counter-ions, using an electrode electrically biased to a voltage of between the predetermined charge level and the first discharge level, to the photoreceptor as a function of the image-wise distribution of charges on the photoreceptor to form a first color image, wherein a second substantially uniform predetermined photoreceptor charge level results such that it is lower than the first predetermined charge level but being sufficiently high to subsequently repel liquid toner in areas not subsequently further discharged; and a transferor to transfer at least the first color image and the second color image to a medium to form the multi-colored image.

The electrophotographic system, as described above, may further include a second image-wise exposing device for exposing the photoreceptor with radiation modulated in accordance with the image data for a second of the plurality of colors in order to partially discharge the photoreceptor to produce an image-wise distribution of charges on the photoreceptor corresponding to the image data for the second of the plurality of colors in registration with the first color image, wherein the second image-wise exposing device produces the image-wise distribution of charges without erasing the photoreceptor subsequent to the first image-wise exposing of the photoreceptor; and a second applicator to apply a second color liquid toner to the image-wise distribution of charges on the photoreceptor to form a second color image in registration with the first color image.

Preferably, a barrier layer in accordance with the present invention has a thickness of about 0.5 micrometers to about 1.3 micrometers and, more preferably, from about 0.8 micrometers to about 1.0 micrometers. In one embodiment, the organic photoreceptor is in a form of a flexible belt.

In accordance with the present invention, an organic photoreceptor may further include a tie layer, wherein the tie layer is positioned between the barrier layer and the release layer. In one embodiment, the tie layer is formed from a tie layer coating composition preferably including a polyetheramine having aromatic ether and amine repeating units in its backbone and pendant hydroxyl moieties. In

another embodiment, the tie layer is formed from a tie layer coating composition preferably including a polyamide. In yet another embodiment, the tie layer is formed from a composition preferably including a polyvinyl acetal and a methylvinyl ether/maleic anhydride copolymer. In a further embodiment, the tie layer is formed from a composition preferably including a polyvinyl acetal, methylvinyl ether/maleic anhydride copolymer, and a crosslinking agent.

The invention provides organic photoreceptors featuring a combination of good mechanical and electrostatic properties. Specifically, photoreceptors in accordance with the present invention possess improved resistance to liquid toner-induced stress crazing under environmental extremes of temperature and humidity and increased protection from damage due to corona-induced charge injection. High quality images produced using a photoreceptor in accordance with the present invention are maintained after repeated cycling.

Brief Description of the Drawings

Figures 1a and 1b are schematic illustrations of embodiments of organic photoreceptors in accordance with the present invention; and

Figure 2 is a schematic illustration of an electrophotographic system including an organic photoreceptor in accordance with the present invention, for producing multi-colored images.

Detailed Description

The present invention provides an organic photoreceptor 10 that preferably includes, as shown in Figure 1a, a conductive substrate 102, a photoconductive element 104, a barrier layer 106, and a release layer 108. In accordance with the present invention, the barrier layer 106 is preferably at least a dual layer including an undercoat 103 and an overcoat 105, wherein the undercoat 103 and the overcoat 105 are formed from coating composition having different components, discussed below.

Preferably, the undercoat 103 is formed on the photoconductive element 104 or a tie layer, as shown in Figure 1b. As shown in Figure 1a, the overcoat layer 105 is formed on the undercoat layer 103, although it is contemplated that there may be one

or more coatings between the undercoat 103 and the overcoat 105. However, in any construction according to the present invention, it is preferable that the overcoat 105 be the upper most coating such that the release layer 108 is formed on the overcoat 105.

5 Preferably, the photoconductive element 104 is a bilayer construction featuring a charge generating layer 110 and a separate charge transport layer 112. The charge generating layer 110 may be located intermediate the conductive substrate 102 and the charge transport layer 112, as shown in Figure 1a. Alternatively, the photoconductive element may be an inverted construction in
10 which the charge transport layer is intermediate the conductive substrate and the charge generating layer, i.e., the locations of layers 110 and 112 are reversed from that show in Figure 1a. The organic photoreceptor may be in the form of a plate, drum, or belt, with flexible belts being preferred.

Referring to Figure 1b, another embodiment in accordance with the present
15 invention is shown, wherein an organic photoreceptor 10' includes a conductive substrate 102, a photoconductive element 104, a barrier layer 106 including an undercoat 103 and an overcoat 105, a tie layer 107, and a release layer 108. Consistent with a photoreceptor construction in accordance with the present invention, one skilled in the art will readily appreciate that other layers (e.g., a
20 charge injection barrier layer) can be present in the photoreceptor.

Photoconductive Element

As mentioned above, a photoconductive element preferably includes a charge generating layer and a charge transport layer. Generally, the charge generating layer
25 includes a charge generating compound dispersed within a binder. The charge generating compound is a material that is capable of absorbing light to generate charge carriers. Examples of suitable compounds are well known and include dyestuffs and pigments (such as metal-free phthalocyanine pigments from Zeneca, Inc., and Y-form metal-free phthalocyanine pigments).

30 Charge transport compounds suitable for use in the charge transport layer of the photoconductors of the present invention should be capable of supporting the

injection of photo-generated holes or electrons from the charge generation layer (depending upon the charging polarity) and allowing the transport of these holes or electrons through the charge transport layer to selectively discharge the surface charge. Preferable hole transport compounds comprise aromatic amines, hydrazone
5 compounds, oxadiazole compounds, oxazole compounds, pyrazoline compounds, triphenyldiamine compounds, and triarylmethane compounds. Particularly preferred transport materials are described in U.S. Pat. App. Ser. No. 09/172,379, filed October 14, 1998, entitled "Organophotoreceptors for Electrophotography Featuring Novel Charge Transport Compounds" (Mott et al.). Polymeric charge transport
10 materials such as polyvinyl carbazole may also be used. Additional materials are disclosed in Borsenberger and Weiss, "Photoreceptors: Organic Photoconductors," Ch. 9, Handbook of Imaging Materials, Ed. Arthur S. Diamond, Marcel Dekker, Inc., 1991.

The charge transport compound may act as a binder. It is also possible to
15 combine the charge transport compound and/or the charge generating compound with a separate polymeric binder. Examples of suitable binders include styrenebutadiene copolymers, modified acrylic polymers, vinyl acetate polymers, styrene-alkyd resins, soya-alkyl resins, polyvinyl butyral, polyvinylchloride, polyvinylidene chloride, acrylonitrile, polycarbonate, polyacrylic and methacrylic
20 esters, polystyrene, polyesters, and combinations thereof. Examples of suitable polycarbonate binders include aryl polycarbonates, such as aryl polycarbonates including poly(4,4-dihydroxy-diphenyl-1,1-cyclohexane) ("Polycarbonate Z 200; Z 300; Z 400; Z 800," all available from Mitsubishi Engineering Plastics, White Plains, NY) and poly(Bisphenol A carbonate)-co-4,4'(3,3,5-trimethyl
25 cyclohexylidene) diphenol.

A particularly useful binder is polyvinyl butyral. This material has free hydroxyl groups available for reaction, e.g., with isocyanate groups which may be present in the charge transport layer, the charge generating layer, additional layers, or a combination thereof.

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Barrier Layer

Without being bound by any particular theory, it is believed that state of the art barrier layers rely on hydrogen-bonding, small intramolecular void volume, or strong dipolar attractions between the neighboring polymer chains to restrict
5 diffusion of toner solvents and/or moisture through polymers with strong intermolecular associations (e.g., polyvinyl alcohol (PVOH)), phenoxy resins, and the like). These polymers can be coated from solvents/water but are known to be less effective barriers in high humidity environments. It is further believed that water vapor and trace toner impurities can increase the diffusion rate of toner
10 solvents, such as that commercially available under the trade designation of NORPAR or ISOPAR through the barrier layer by swelling the polymer lattice and providing a path for toner solvent diffusion.

Additionally, although barrier layers included in photoreceptors are well known, they do not possess or are inadequate in one or more of the following
15 performance characteristics: (a) providing sufficient protection to the organic photoreceptor from damage due to corona-induced charge injection; (b) substantially inert with respect to the organic photoconductive layer; (c) exhibiting sufficient resiliency to withstand shear, compressional, and tensional forces exerted on the belt as it passes through the system (described below) when the photoreceptor is used in
20 an endless belt form; and (d) providing sufficient protection to limit or prevent a liquid toner from contacting the organic photoconductor. For example, conventional barrier layers are typically formed from materials such as crosslinkable siloxanol-colloidal silica, a dispersion of hydroxylated silsesquioxane and colloidal silica in an alcohol medium, a polymer resulting from a mixture of polyvinyl alcohol with
25 methyl vinyl ether/maleic anhydride copolymer, an organic polymer (e.g., polyacrylates, polyurethanes, polyvinyl acetals, sulfonated polyesters, mixtures of polyvinyl alcohol with methylvinylether/maleic anhydride copolymer and silica, and methyl cellulose) and polyvinyl butyral crosslinked with methylvinylether/maleic anhydride copolymer. However, many of these barrier layers may not possess the
30 necessary resistance to the paraffinic solvents used in liquid toners (solvents such as NORPAR and ISOPAR from Exxon, USA) to protect the organic photoreceptor

from the solvent in the liquid toner while maintaining suitable electrostatic and print quality properties.

In accordance with the present invention, an organic photoreceptor includes a barrier layer comprising an undercoat and an overcoat on the undercoat. According to the present invention, the undercoat should, by itself, exhibit good toner solvent resistance at relatively low humidity conditions, e.g., less than about 50% relative humidity, evaluated as described in the Examples herein.

One suitable undercoat is formed from an undercoating composition including a poly(vinyl alcohol), a methylvinyl ether/maleic anhydride copolymer, and an aldehyde based crosslinker. One suitable poly(vinyl alcohol) is commercially available under the trade designation AIRVOL 165, from Air Products and Chemicals, Inc., Allentown PA. The polyvinyl alcohol AIRVOL series, 165 grade was chosen for its high hydrocarbon and water resistance properties that are imparted by its high molecular weight and high degree of hydrolyzation. One suitable methylvinyl ether/maleic anhydride copolymer is commercially available under the trade designation of GANTREZ AN series, from ISP Chemical, Wayne, NJ. Suitable aldehyde based crosslinkers can include a simple dialdehyde crosslinker (e.g., Glyoxal 40 from Aldrich Chemical Corp., Milwaukee, WI) or higher aldehyde crosslinkers (e.g., glutaraldehyde and hydroxyadipaldehyde from Aldrich Chemical Corp., Milwaukee, WI).

Another suitable undercoat is formed from the addition polymerization of two acrylate monomers (2-hydroxyethyl methacrylate (HEMA) and 2-hydroxyethyl acrylate (HEA)) with itaconic acid (ITA) and using azobis-isobutyronitrile (AIBN) as the initiator. The monomers and initiator are available from Aldrich Chemical Corp., Milwaukee, WI. As a portion of the polymer, the polar hydroxyl moiety of the two acrylates imparts resistance to the non-polar toner solvent while the itaconic acid is free to crosslink with these groups and increases the adhesion of the barrier to the adjacent layers.

According to the present invention, a suitable overcoat is formed from an overcoating composition including a material selected from the group consisting of an amine-containing hydroxyether, an amide-containing hydroxyether, and a

combination thereof. By themselves, barrier layers formed from these materials are known to be suitable gas barriers, particularly above 60% relative humidity.

However, when used in an electrophotographic system, barrier layers (including these materials) are less effective in preventing diffusion of toner solvent and water

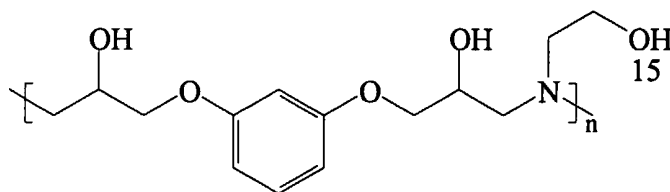
5 vapor to the organic photoconductor, particularly in a relatively high humidity environment (i.e., greater than 50% relative humidity). However, this overcoat layer

is more effective than most hydrocarbon barrier materials presumably due to the aromatic portion of the polymer. Some suitable amine- and amide-containing

hydroxyethers for use as an overcoat include those of the following structures:

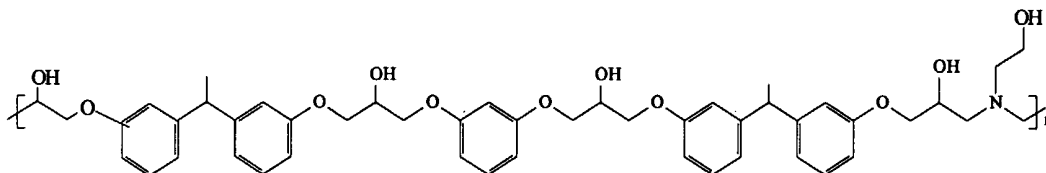
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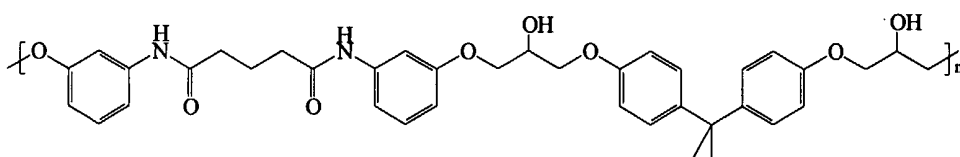
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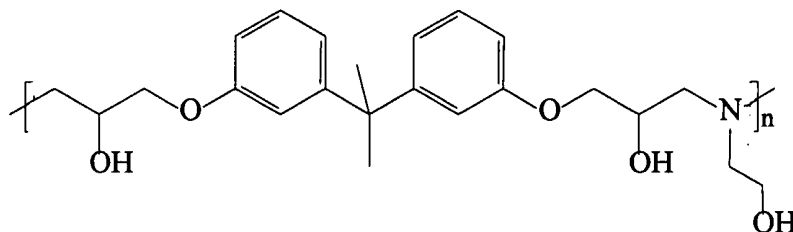
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IV:

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Polymers of Structures I-IV can be prepared by methods described in references U.S. Pat. Nos. 5,491,204 and 5,464,924. Structure IV is commercially available under the trade designation BLOX, from Dow Chemical Co. These overcoat layers can also be used as the undercoat layer provided that the coating solvent does not degrade the organic photoconductor (e.g., a mixture of tetrahydrofuran and methoxy-2-propanol).

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A barrier layer including an undercoat and an overcoat preferably has a total thickness (i.e., the thickness of the undercoat plus the thickness of the overcoat) sufficient to enhance protection of the organic photoconductor from the solvent typically included in the toner (as indicated by the reduction of cracks or crazing in an organic photoreceptor after testing as described herein) while simultaneously providing sufficient protection to the organic photoreceptor from damage due to electrostatic cycling fatigue (as indicated by the voltage from the laser charge up and discharge tests described herein). Preferably, the barrier layer has total thickness of about 0.5 micrometers to about 1.3 micrometers, where the undercoat preferably has a thickness of about 0.2 micrometers to about 0.7 micrometers, while the overcoat preferably has a thickness of about 0.2 micrometers to about 0.6 micrometers.

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Preferably, the 2-hydroxyethyl methacrylate (HEMA), is included in the undercoating composition in an amount from about 10 to about 80 wt.%. Preferably, the 2-hydroxyethyl acrylate (HEA), is included in the undercoating composition in an amount from about 0 to 70 wt.%. Preferably, the itaconic acid (ITA), is included in the undercoating composition in an amount from about 0 to about 70 wt.%.

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In another preferred embodiment, the undercoating composition comprises a ratio of the poly(vinyl alcohol) to the copolymer of about (1:1) and, more preferably, the ratio of the poly(vinyl alcohol) to the copolymer is about (10:1). The amount of aldehyde cross linking agent added to the binder system was between 0-25% of the solids by weight, more preferably between 6-16 wt% of the solids. Colloidal silica (e.g., those commercially available under the trade designations NALCO 1034 or NALCO 2326 from the Nalco Chemical or the SNOTEX series from Nissoon Chemicals) can be present in an amount between 0-45 wt.% of the solids by weight, more preferably between 25-35 wt.% of the solids.

Preferably, the poly(vinyl alcohol) is included in the undercoating composition in an amount from about 30% and, more preferably from about 45% of the solids by weight, to an amount of about 100%, preferably to about 70%, of the poly(vinyl alcohol) in the undercoating composition. Even more preferably, the undercoating composition includes from about 50% to about 65% solids by weight of the poly(vinyl alcohol).

Preferably, the copolymer is included in the undercoating composition in an amount less than about 50% solids by weight, more preferably less than about 17% and, preferably, more than about 0% solids by weight, and more preferably about 3% solids by weight of the copolymer in the undercoating composition.

Preferably, the crosslinking agent is included in the undercoating composition in an amount less than about 40% solids by weight, more preferably less than about 30% and, preferably, more than about 0% solids by weight, and more preferably about 10% solids by weight of the crosslinking agent in the undercoating composition.

Preferably, the colloidal silica is included in the undercoating composition in an amount less than about 50% solids by weight, more preferably less than about 30% and, preferably, more than about 0% solids by weight, and more preferably about 10% solids by weight of the colloidal silica in the undercoating composition. Most preferably, the undercoating composition includes about 27% solids by weight of the colloidal silica in the undercoating composition.

As mentioned above, a suitable overcoating composition includes a material selected from the group consisting of an amine-containing hydroxyether, an amide-containing hydroxyether, and a combination thereof. Preferably, the hydroxyether is present in the overcoating composition in an amount greater than 75%, more preferably about 100 % solids by weight of the hydroxyether. Colloidal silica can make up the balance of the solids in the formulation.

Optional Components

Other optional components may be added to the barrier layer coating composition including surfactants, plasticizers, anti-static agents, wetting agents, anti-foaming agents, conductive additives, and fillers, to name a few, so long as the barrier layer characteristics (such as those mentioned above) are not impaired. One preferred optional component is a surfactant, preferably a nonionic surfactant, such as that commercially available under the trade designation TRITON X-100, from Aldrich Chemical, Milwaukee, WI. If present, the surfactant is preferably in a barrier layer coating composition in an amount preferably from about 0.0001% to about 1.0%, more preferably from about 0.01% to about 0.05%, and, even more preferably, from about 0.02% to about 0.03% by weight.

Another preferred optional component is silica particles. The silica particles preferably are colloidal silica having average diameter from 5 to 200 nm. As used herein, "colloidal silica" refers to a dispersion of silicon dioxide particles in which the silica particles can range in size from about 5 to about 30 nm. Suitable colloidal silica is commercially available under the trade designations NALCO 1034 and NALCO 2326 both from Nalco Chemical Co. Chicago IL, and SNOTEX O, from Nissan Chemical Industries, Ltd., Tarrytown, NY, for example. Preferably, the colloidal silica is present in an undercoating and/or overcoating composition in an amount of less than about 50 wt.%, more preferably, less than about 40 wt.%, and even more preferably from about 30 wt.% to about 20 wt. % of total solids.

Suitable conductive additives include conductive pigments, conductive polymers, doped conductive polymer compositions such as conductive organic molecules, and conductive pigments (or conductive particles). The amount of

conductive additive is preferably less than 40%, more preferably less than about 30% by weight of the barrier layer.

Preferably, a barrier layer coating composition is applied to an organic photoconductor using any conventional coating technique, such as air doctor coating, blade coating, air knife coating, squeeze coating, reverse roll coating, transfer roll coating, gravure coating, kiss coating, cast coating, spray coating, dip coating, bar coating, extrusion coating, die coating (including slot die coating), for example. Preferably, the barrier layer coating composition is applied to an organic photoconductor at a thickness such that a barrier layer formed has a dry thickness from about 0.2 micrometers to about 0.8 micrometers.

Surprisingly, it was found that organic photoreceptors including such barrier layers exhibited improved resistance to solvent while maintaining suitable charge-discharge properties under testing conditions equivalent print cycles in the thousands, as exemplified herein. Advantageously, it was found that a barrier layer formed from a barrier layer coating composition including poly(vinyl alcohol), a methylvinylether/maleic anhydride copolymer, and crosslinking agent or a HEMA:ITA:HEA terpolymer exhibited decreased crazing when exposed to the toner solvent and improved electrostatic characteristics as compared to a conventional barrier layer, such as a barrier layer containing methyl cellulose and maleic anhydride, as is described in U.S. Pat. No. 5,124,220 (Brown et al.). Furthermore, it was surprisingly found that the addition of the cross-linker improved adhesion of the barrier layer to the charge generating layer of the organic photoconductor without adversely affecting the electrostatic characteristics of the photoreceptor, as is demonstrated herein.

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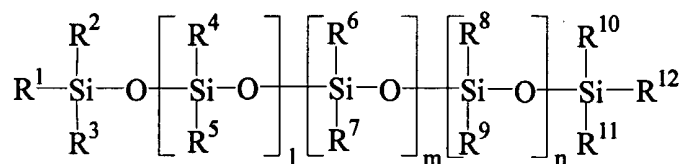
Release layers

A release layer is typically applied over the barrier layer and must adhere well to the barrier layer, preferably without the need for adhesives. Additionally, the release layer must not significantly interfere with the charge transport characteristics of the photoreceptor. Conventional release layers are formed from a variety of well known materials including fluorinated polymers (such as those described in U.S. Pat.

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Nos. 4,996,125 and 5,723,242, for example), siloxane polymers, silanes, silicone polymers (such as that described in U.S. Pat. No. 4,600,673, for example), polyethylene, and polypropylene, to name a few. Other suitable compositions for forming a release layer including a siloxane polymer with a low content of functional groups capable of crosslinking are described in U.S. Patent No. 5,652,078 (Jalbert et al.) and in copending U.S. Patent Application Ser. No. 09/504,461, filed February 16, 2000 (Li et al.).

In one preferred embodiment, a release layer includes a composition including (a) from zero to about 30 parts by weight of a polymer having the formula



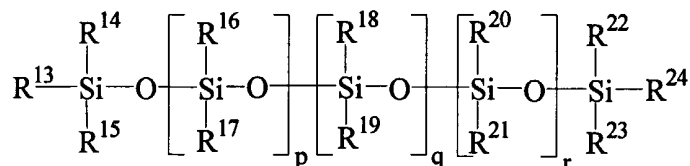
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wherein R^1 , R^2 , R^3 , R^6 , R^7 , R^{10} , R^{11} , and R^{12} are each independently selected from an alkyl group, an alkenyl group, an aryl group, and an aralkyl group, such that at least one of R^6 and R^7 is an alkenyl group, R^4 , R^5 , R^8 , and R^9 are each independently selected from an alkyl group, an aryl group, and an aralkyl group,

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l , m , and n are each independently integers so long as the polymer contains greater than 3 mol% vinyl-containing siloxane groups;

(b) more than about 20 parts by weight of a polymer selected from the group of



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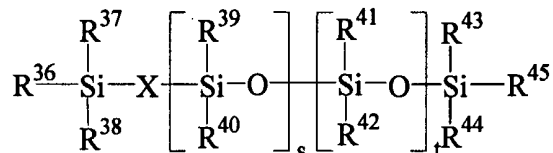
wherein R^{13} , R^{14} , R^{15} , R^{18} , R^{19} , R^{22} , R^{23} , and R^{24} are each independently selected from an alkyl group, an alkenyl group, an aryl group, and an aralkyl group, such that at least two of R^{13} , R^{14} , R^{15} , R^{18} , R^{19} , R^{22} , R^{23} , and R^{24} alkenyl groups,

R^{16} , R^{17} , R^{20} , and R^{21} are each independently selected from an alkyl group, an aryl group, and an aralkyl group,

25

p, q, and r are each independently integers so long as the polymer has less than 3 mol% vinyl-containing siloxane groups; a (vinyl siloxy)(siloxo)-modified silica having a vinyl content of less than about 0.6 vinyl equivalent/kg; and a combination thereof; and

5 (c) greater than about 0 parts to about 20 parts by weight of a cross-linking agent of the formula



wherein R³⁶, R³⁷, R³⁸, R⁴³, R⁴⁴, and R⁴⁵ are each independently selected from hydrogen, an alkyl group, an aryl group, and an aralkyl group,

10 R³⁹, R⁴⁰, R⁴¹, and R⁴² are each independently selected from hydrogen, an alkyl group, and an aryl group,

X is O, or a divalent organic linking group, and

s and t are independently integers so long as there are at least two functional groups capable of cross-linking per molecule.

15

Tie layers

Optionally, an organic photoreceptor in accordance with the present invention can have a structure including an organic photoconductor, a barrier layer (as described above), a tie layer, and a release layer. In one embodiment, the tie layer can be positioned between the barrier layer and the release layer to enhance adhesion of the release layer to the barrier layer in the organic photoreceptor. In another embodiment, the tie layer can be positioned between the charge generating layer and the barrier layer to enhance adhesion of the barrier layer to the organic photoconductor. One with ordinary skill in the art will readily appreciate that an organic photoreceptor according to the present invention may possess a variety of layered configurations, such as the presence of a tie layer between the release layer and the barrier layer as well as the presence of a tie layer between the charge generating layer and the barrier layer.

25

Preferably, a tie layer is formed from a tie layer coating composition comprising an organic polymer. The term "organic polymer" refers to a material that is formed from a carbon chain or ring structure containing hydrogen and, optionally, heteroatoms such as sulfur, oxygen, nitrogen, and a combination thereof.

5 Preferably, an organic polymer suitable for use in the present invention include those selected from the group of polyetheramines, polyvinyl acetals, polyamides, methylvinyl ether/maleic anhydride copolymer, and combinations thereof. Preferably, an organic polymer is present in a tie layer coating composition in an amount of less than about 30% solids in the tie layer coating composition.

10 One preferred type of organic polymer for use in a tie layer in accordance with the present invention is a polyetheramine having aromatic ether/amine repeating units in its backbone and pendant hydroxyl moieties. Namely, a suitable polyetheramine is preferably formed by reacting diglycidyl ethers of dihydric aromatic compounds (e.g., the diglycidyl ether of bisphenol-A, hydroquinone, or
15 resorcinol) with amines, preferably having no more than two amine hydrogens per molecule (e.g., piperazine or ethanolamine), as is described in U.S. Pat. No. 5,275,853 (Silvis et al.). Preferred polyetheramines are commercially available under the trade designation series BLOX from The Dow Chemical Company, Midland, MI.

20 Another preferred type of organic polymer for use in a tie layer in accordance with the present invention is a polyamide, preferably, a soluble polyamide as is known in the art. For example, suitable polyamide materials are commercially available under the trade designations ULTRAMID, from BASF Corporation, Mount Olive, NJ; and AMILAN, from Toray Ltd., Japan. Preferably, the polyamide
25 is included in a tie layer coating composition in an amount of less than about 10%, more preferably, less than about 7.5%, and even more preferably, less than about 5% by weight.

Yet another preferred type of organic polymer for use in a tie layer in accordance with the present invention is a mixture of a polyvinyl acetal, preferably
30 polyvinyl butyral, with a methylvinyl ether/maleic anhydride copolymer, in which the ratio of polyvinyl acetal to methylvinyl ether/maleic anhydride copolymer is

preferably from about 5:1 to about 15:1 and, more preferably, about 12:1.

Preferably, the mixture of a polyvinyl acetal with methylvinyl ether/maleic anhydride copolymer is included in a tie layer coating composition in an amount of less than about 10%, more preferably, less than about 7.5%, and even more preferably, less than about 5% by weight. Optionally, a coupling agent can be included and is preferably selected from the group of glycidoxy-propyltrimethoxysilane, vinyltrimethoxysilane, chloromethyltrimethoxysilane, methyltrimethoxysilane, and 3-aminopropyltriethoxysilane. If present, the coupling agent is typically present in an amount less than about 5% by weight of the tie layer coating composition.

A further preferred type of organic polymer for use in a tie layer in accordance with the present invention is a mixture of a polyvinyl acetal, preferably polyvinyl butyral, and a cross-linking agent, preferably, a bis aldehyde, more preferably, an aliphatic dialdehyde, and, even more preferably, glyoxal, such as that commercially available under the trade designation GLYOXAL 40, from Aldrich Chemical, Milwaukee, WI. Preferably, the mixture of a polyvinyl acetal with a cross-linking agent is included in a tie layer coating composition in an amount of less than about 10%, more preferably, less than about 7.5%, and even more preferably, less than about 5% by weight.

Preferably, a tie layer coating composition also includes silica, preferably colloidal silica. Preferred colloidal silica compositions are commercially available under the trade designations SNOTEX O, from Nissan Chemical Industries, Ltd., Tarrytown, NY, and CABOSIL TS-720 from Cabot Corp., Tuscola, IL. The tie layer coating composition preferably includes colloidal silica in an amount of about 0 to about 12% by weight.

In accordance with the present invention, a tie layer coating composition is applied to at least one surface on the organic photoconductor, such as on the surface of the charge generating layer, the surface of the barrier layer, or both. Regardless of the surface on which the tie layer coating composition is applied, the resulting tie layer preferably has a thickness of about 0.05 micrometer to about 0.7 micrometer.

Electrophotographic System

Organic photoreceptors described above are suitable for use in an imaging process with either dry or liquid toner development. Liquid toner development is generally preferred because it offers the advantages of providing higher resolution
5 images and requiring lower energy for image fixing compared to dry toners. Examples of useful liquid toners are well known. They typically include a colorant (preferably a pigment), a resin binder, a charge director, and a carrier liquid. A preferred resin to colorant ratio is 2:1 to 10:1, more preferably 4:1 to 8:1. Typically, the colorant, resin, and the charge director form the toner particles.

10 Organic photoreceptors according to the invention are particularly useful in a compact electrophotographic imaging system where an organic photoreceptor in accordance with the present invention is wound around and supported by several rollers. A number of apparatus designs may be employed, including for example, the apparatus designs disclosed in U.S. Patent Nos. 5,650,253 (Baker et al.);
15 5,659,851 (Moe et al.); and 5,916,718 (Kellie et al.).

Figure 2 is a schematic illustration of one preferred embodiment of an electrophotographic system 42 and a method for producing a multi-colored image utilizing an organic photoreceptor described above. An organic photoreceptor 10, preferably in the form of an endless belt, is mechanically supported by belt 44 that
20 rotates, preferably in a clockwise direction, around rollers 46 and 48. The organic photoreceptor 10 may be first conventionally erased with an erase lamp 14. Preferably, any residual charge left on the organic photoreceptor 10 after the preceding cycle is removed by the erase lamp 14 and then conventionally charged using charging device 18 (e.g., a corona charging device), such procedures being
25 well known in the art. When charged, a surface of the organic photoreceptor 10 is preferably charged from about 550 volts to about 750 volts. A laser scanning device 50 exposes the charged surface of the organic photoreceptor 10 to radiation in an image-wise pattern corresponding to a first color plane of the image to be reproduced. Suitable laser scanning devices are well known in the art.

30 Thereafter, charged pigment particles in a liquid toner 54, corresponding to the first color plane, will migrate to and plate upon the charged surface of the

organic photoreceptor 10 in areas where the surface voltage of the organic photoreceptor 10 is less than the bias of electrode 56 associated with a liquid toner developer station 52. Charge neutrality of the liquid toner 54 is maintained by negatively charged counter ions that balance the positively charged pigment particles. The counter ions are deposited on the surface of the organic photoreceptor 10 in areas where the surface voltage is greater than the bias voltage of the electrode 56, such as that described in U.S. Pat. No. 5,596,398 (Woo et al.), associated with the liquid toner developer station 52. One example of a suitable developer station is described in U.S. Pat. No. 5,300,990 (Thompson et al.). Another developer apparatus is described in U.S. Pat. No. 5,758,236 (Teschendorf et al.).

At this stage, the organic photoreceptor 10 includes, on its surface, an image-wise distribution of plated "solids" of liquid toner 54 in accordance with the first color plane. The surface charge distribution of the organic photoreceptor 10 has also been recharged with plated ink particles as well as with transparent counter ions from the liquid toner 54, both being governed by the image-wise discharge of the organic photoreceptor 10 due to laser scanning device 50. Thus, the surface charge of the organic photoreceptor 10 is quite uniform. Although not all of the original surface charge of the organic photoreceptor may have been obtained, a substantial portion of the previous surface charge of the organic photoreceptor has been recaptured. With such solution recharging, the organic photoreceptor 10 can be processed for the next color plane of the image to be reproduced.

Although not required, a "topping corona" (not illustrated) may be applied to photoreceptor 10 following the first three or, optionally, all development stations 52, 60, 68 and 76, respectively. For example, while photoreceptor 10 recharges following development with liquid inks 54, 62 and 70, it typically does not recharge completely to the previously charged voltage. Thus, a conventional corona charging device may be employed following development stations 52, 60 and 68 to bring the voltage on photoreceptor 10 back to a preferred charging level. For example, following erasure by erase lamp 14, the surface of photoreceptor 10 is at a relatively low voltage level, typically around 100 volts. Following charging by a corona charging device 18, the surface of photoreceptor 10 is charged to a relatively high

value suitable to development of a liquid ink, typically around 700 volts. Following image-wise exposure to radiation by laser scanning device 50, corresponding to a first color plane (preferably yellow), the areas of the surface of photoreceptor 10 are discharged to a discharged level of around 150 volts. Non-exposed areas of the surface of photoreceptor 10 remain at a highly charged level, around 700 volts. Following development by developer station 52, the surface of photoreceptor 10 is substantially uniformly charged to an intermediate level of around 500 volts. Discharged areas of photoreceptor 10 are developed "up" to 500 volts and non-discharged areas of photoreceptor 10 are developed "down" to 500 volts. Because this developed voltage will tend to decay over time, a topping corona is preferably used to bring the surface of photoreceptor 10 back up to the high level of around 700 volts.

As the belt 44 continues to rotate, the organic photoreceptor 10 next is image-wise exposed to radiation from laser scanning device 58 corresponding to a second color plane. Significantly, this process occurs during a single revolution of the organic photoreceptor by the belt 44 and without erasing the organic photoreceptor 10 subsequent to exposure to the laser scanning device 58 and the second liquid toner development station 60 corresponding to the first color plane. The remaining charge on the surface of the organic photoreceptor 10 is subjected to radiation corresponding to a second color plane. This produces an image-wise distribution of the surface charge on the organic photoreceptor 10 corresponding to the second color plane of the image.

The second color plane of the image is then developed by a developer station 60 containing a liquid toner 62. The liquid toner 62 preferably contains "solid" color pigments consistent with the second color plane and substantially transparent counter ions that, although they may have differing chemical compositions than the substantially transparent counter ions of the liquid toner 54, they are still substantially transparent and oppositely charged to the "solid" color pigments. The electrode 64 provides a bias voltage to allow "solid" color pigments of the liquid toner 62 to create a pattern of "solid" color pigments on the surface of the organic photoreceptor 10 corresponding to the second color plane. The transparent counter

ions also substantially recharge the organic photoreceptor 10 and make the surface of the organic photoreceptor 10 substantially uniform so that another color plane may be placed upon the organic photoreceptor 10 without erasing or corona discharging.

5 A third color plane of the image to be reproduced is deposited on the surface of the photoreceptor 10 in a similar fashion using a laser scanning device 66 and a developer station 68 containing a liquid toner 70 using an electrode 72. Again, the surface voltage of the photoreceptor 10 may be somewhat less than existed prior to exposure to the laser scanning device 66 but will be substantially “recharged” and
10 will be quite uniform allowing application of the fourth color plane without erasing or corona charging.

 Similarly, a fourth color plane is deposited upon the photoreceptor 10 using a laser scanning device 74 and a developer station 76 containing a liquid toner 78 using an electrode 80.

15 Preferably, excess toner from the liquid toners 54, 62, 70, and 78 is “squeezed” off using a roller that may be used in conjunction with one or more of the developer stations 52, 60, 68, and 76, (shown as rollers 82, 84, 86, and 88, respectively, as described in U.S. Pat. No. 5,754,928 (Moe et al.)) to form plated
20 solids from each of the liquid toners. The plated solids on the photoreceptor are then dried using a drying mechanism 34 to form a completed dry four color image. The drying mechanism 34 may utilize air blowers or may be other active devices such as drying rollers, vacuum devices, coronas, etc. One suitable drying mechanism is described in U.S. Pat. No. 5,420,675 (Thompson et al.).

 The dry four color image is then preferably transferred, either directly to a
25 medium 36 to be printed, or more preferably, indirectly by way of transfer mechanism 39, as shown in Figure 2. Typically, heat and/or pressure are used to fix the image to the medium 36. Although the transfer mechanism 39 can take a variety of forms, one suitable transfer mechanism includes transfer rollers 38 and 40 and is described in U.S. Pat. No. 5,650,253 (Baker et al.).

30 With proper selection of charging voltages and liquid toners, the process may be repeated an indeterminate number of times to produce a multi-colored image

having an indeterminate number of color planes. Although the process and apparatus has been described in connection with four color images, one skilled in the art will appreciate that the present invention is suitable for multi-color images having two or more color planes.

5 The following examples are illustrative of specific embodiments and/or methods according to the present invention. A wide variety of variations from the following examples are within the scope of the present invention and are only to be limited by the appended claims.

10

Examples

Preparation of barrier layer coating compositions:

1. Barrier Samples

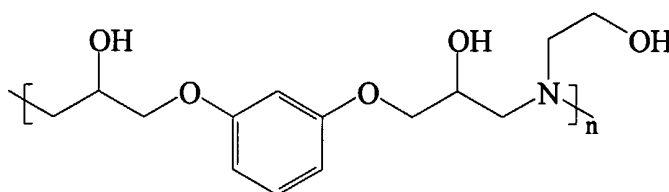
15

The following polymers were examined for use as single layer barriers.

(A) Amide/Amine Containing Hydroxy Ether Polymers

Sample 1

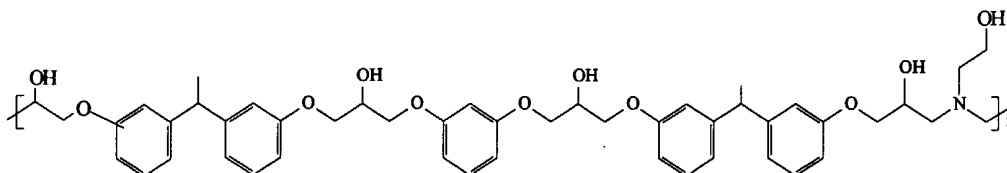
20



25

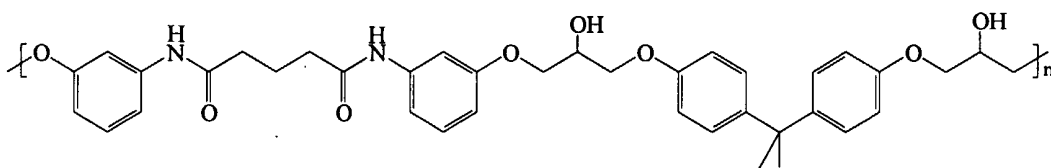
Sample 2

30



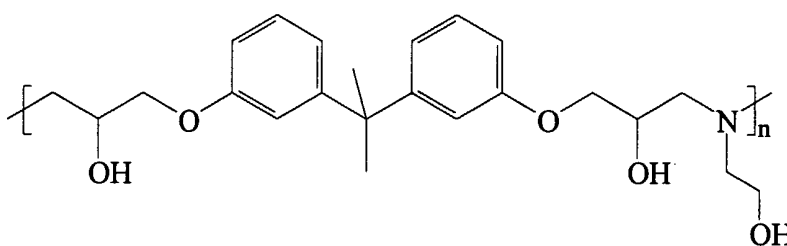
35

Sample 3



5

Sample 4



10 Polymers from Samples 1-3 can be prepared by methods described in references U.S. Pat. Nos. 5,491,204 and 5,464,924, and 5,275,853 and Brennan et al, *Macromolecules*, 1995, **28**, 6694, *ibid* 1996, **29** 3715, Sample 4 was obtained directly from Dow Chemical Co. - BLOX series of polymers.

15 (B) Phenoxy Resin and Poly(vinyl alcohol), formulation details shown in Table 1 below.

Sample 5: A phenoxy resin commercially available under the trade designation PAPHEN, from Phenoxy Resin Associates

20 Sample 6: Poly(vinyl alcohol) commercially available under the trade designation AIRVOL 165 from Air Products Inc.

Sample 7: PVOH / Gantrez AN 169 with 10 wt% Nalco 1034 colloidal silica, coated from 1-3 wt% solids in water

Sample 8: PVOH / Gantrez AN 169 without the colloidal silica, coated from 1-3 wt% solids in water

25 Sample 9: PVOH / Gantrez AN 169 / Glyoxal (40 wt% dialdehyde

crosslinker in water from Aldrich Chemical) / colloidal silica Nalco 2326 coated from 3 wt% solids in water/methanol

Sample 10: A barrier layer made from PVOH / Gantrez AN 169 / Triton X-100 surfactant / 3-glycidoxypropyl-trimethoxysilane (GPS) coupling agent and a much higher Nalco 2326 colloidal silica content, described by E. Woo et al., (WO 95/02853).

TABLE 1
SUMMARY OF PVOH FORMULATIONS AND COATING CONCENTRATION

Sample	PVOH wt%	Gantrez wt%	Silica wt%, type	Glyoxal wt%	GPS wt%	Triton X-100 wt%	Solids wt%
6	100	0	0%	0	0	0	3
7	45	45	10%, Nalco 1034	0	0	0	1-3
8	50	50	0%	0	0	0	1-3
9	52	5	27%, Nalco 2326	16	0	0	3
10	34	3	44%, Nalco 2326	0	15	4	3

10

(C) Hydroxyacrylate Polymers – Samples 11-16

Several acrylate polymers have been synthesized using 2-hydroxyethyl methacrylate (HEMA), itaconic acid (ITA), and 2-hydroxyethyl acrylate (HEA) and azobis-isobutyronitrile (AIBN) as the initiator in methanol for 20-48 hr. at 60°C under a nitrogen blanket. Polymers were purified by precipitating 3 times in a (1:1) mixture of 2-butanone and Norpar 12. The following table lists the monomer weight ratios used to charge the reaction vessels.

20

TABLE 2
STARTING REACTOR MONOMER WEIGHT RATIOS

Sample	HEMA	ITA	HEA
11	70	15	15
12	15	70	15
13	15	15	70

14	33	33	33
15	75	0	25
16	80	20	0

Application of barrier layer coating compositions on to a photoconductor:

An inverted dual layer organic photoconductor (herein, "OPC") was prepared as described in U.S. Pat. App. Ser. No. 09/172,379, filed October 14, 1998, entitled "Organophotoreceptors for Electrophotography Featuring Novel Charge Transport Compounds" (Mott et al.) was used as the substrate, that included a polyester layer, an aluminum layer, a PET layer (formed from a resin commercially available under the trade designation VITEL PE 2200, from Bostik Chemicals, Middleton, MA, at a 4.4% solids in a 2:1 MEK:toluene mixture, coated at a thickness of 0.2 micrometers using a slot die coater with a web speed of 3.048 meters/min., dried in 4 oven zones of 110°C, 120°C, 140°C, and 150°C), a charge transport layer of a thickness of about 9.0 micrometers, and a charge generating layer of a thickness of about 0.3 micrometers. A barrier layer coating composition was then coated over the charge generating layer at a thickness of about 0.3-1.0 microns.

The charge transport layer (CTL) was composed of either a hydrazone (Hydr) or a triphenyl diamine (TPD) as the charge transport material in a polymeric binder, as follows:

(1) The Hydr CTL was composed of a 1:1 ratio of N-ethyl-carbazolo-3-aldehyde-N-methyl-N-phenyl-hydrazone to N-ethyl,-carbazolo-3-aldehyde-N,N-diphenyl-hydrazone (both from H.W. Sands) with Polycarbonate Z200 binder (from Mitsubishi Gas Chemical Co.) comprising the other 50 wt% of the total solids.

(2) The TPD CTL was composed of either 40 wt% or 50 wt% of N,N'-diphenyl-N,N'-bis(3-methylphenyl)(1,1'-biphenyl)-4,4'-diamine (from H.W. Sands) in the Polycarbonate Z200 binder (remaining solids portion). While not wishing to be bound by any particular theory, it is believed that an OPC including TPD CTLs are more sensitive to toner solvent-induced environmental stress crazing than an OPC including a hydrazone-based CTL and, thus, provides a more sensitive test of barrier layer effectiveness.

The barrier layer coating compositions described above were from 1-8 wt% solids solutions in the solvent, as summarized below in Table 4, were coated either by hand knife edge or meyer bar for screening purposes, or preferably, on a web using as slot die coater (relative humidity of the web was constant at 40%) for detailed evaluations to give a dry coating thickness of 0.3-1.0 μm . These coatings were applied directly on top of an organic photoconductor (OPC) built from the following layers: aluminized polyester, charge transport layer (9 μm), and a charge generating layer (0.3 μm). A low surface energy, crosslinked silicone resin containing 0.1 wt. % colloidal silica was coated on top of the barriers to complete the organic photoreceptor (OPR) construction. The web coated OPC was passed through 4 oven zones set at 90°C, 100°C, 110°C, and 120°C to dry the barrier layer coating composition, forming the barrier layer. Once the barrier and release layers were formed on the OPC, it is referred to herein as an OPR (organic photoreceptor).

15 **Testing of OPR Examples and Comparative Examples:**

1. Dynamic Carrier Liquid Crazing Resistance: A 7.62 cm x 22.86 cm sample of each OPR was mounted on a flexure fatigue tester that applies 50 lbs (24.7 kg) tensile load on the sample. A sufficient amount of a paraffinic hydrocarbon solvent commercially available under the trade designation NORPAR 12, from Exxon Corp., Houston TX, was then spread onto the surface, and six rollers of 2.54 cm diameter continuously deflect the sample from the back side. After 4 hours (which is believed to be equivalent to 10,000 cycles in a belt printing mechanism), the sample is released and visibly examined for any sign of crazing.

25 **2. Static Solvent Crazing Resistance:** A cylindrical sample (30.cm long X 30 cm circumference) of each OPR was mounted on a static load tester, which employs a 1.27 cm and 1.91 cm diameter metal bar on either end of the frame to stretch the sample with 36 lbs (16.33 kg) of force. A sufficient amount of the NORPAR solvent was spread on the coated surface. After 10 minutes, the sample was released, allowed to dry, and visibly examined for signs of crazing according to the subjective standard: a rating of 1 indicated no crazing present, 1.5 indicated very,

30

very light crazing was present, 2 indicated very light crazing, and so on to an upper score of 8 that indicated very heavy crazing. A value more than about 3 was considered an unacceptable to be useful in an electrophotographic process.

- 5 **3. Adhesion to CGL layer:** Two 30.48 cm X 30.48 cm samples of each OPR were cut. A piece of book tape was then stuck onto one sample and rubbed with the thumb. The tape is then pulled back sharply at about 180 degrees. The surface was then visually examined for delamination.

The second sample cut from each OPR was soaked in the carrier liquid
10 overnight at room temperature, dried, and then a piece of book tape was then stuck onto one sample and rubbed with the thumb. The tape is then pulled back sharply at about 180 degrees. The surface was again visually examined for delamination.

- 4. Dry Electrostatic Performance:** Three belts, each measuring 50 cm long by 8.8
15 cm wide, were fastened side-by-side and completely around an aluminum drum (50 cm circumference). The drum rotated at a rate of 7.6 cm /min and the erase, corona charging, laser discharge, stations are located at 20°, 35°, and 45° positions, respectively, from the top of the drum. The first electrostatic probe (Trek 344 electrostatic meter, from Trek Inc., Medina NY) is located immediately after the
20 laser discharge stations and the second probe at 180° from the top of the drum. These measurements were performed at room temperature (25°C).

Electrostatic measurements were obtained from the following sequence of test subroutines:

- 1) **PRODSTART:** This test was designed to evaluate the electrostatic cycling
25 of a new, fresh belt. The belt was completely charged for three cycles (drum rotations); discharged with the laser at 780nm, 600dpi on the fourth cycle; completely charged for the next three cycles; discharged with only the erase lamp at 720nm on the eighth cycle; and, finally, completely charged for the last three cycles.
- 2) **VLOGE:** This test measured the response of the photoconductor to various
30 irradiation levels (0.01 mW to 3 mW) by monitoring the discharge voltage of the belt as a function of the laser power. A semi-logarithmic plot was generated

(voltage verses log E) when the belt is charged and then discharged using the laser at different power levels.

3) DARK DECAY: This test measured the loss of charge acceptance with time without laser or erase illumination and can be used as an indicator of i) the injection
5 of residual holes from the charge generation layer to the charge transport layer, ii) the thermal liberation of trapped charges, and iii) the injection of charge from the surface or aluminum ground plane. After the belt was completely charged, it was stopped under the probe near the laser discharge station, and the surface voltage level was measured over a period of 90 seconds. The decay in the initial voltage was
10 plotted verses time.

4) LONGRUN: The belt was electrostatically cycled, according to the following sequence for each belt-drum revolution, for 4,000 drum revolutions: the belt was charged by the corona, the laser was cycled on and off to discharge a portion of the belt, and, finally, the erase lamp discharged the whole belt in
15 preparation for the next cycle. The laser was cycled so that the first 16.7 cm of the belt was never exposed, the following 8 cm section was exposed, then 4 cm was unexposed, the next 8 cm section was exposed, and finally the last 12.5 cm was unexposed. This pattern was repeated for 4,000 drum revolutions and the data was collected during the first cycle and then after each 200th drum revolution.

20 5) After the 4,000th cycle (long run test), the PRODSTART (now called PRODEND), VLOGE, DARK DECAY tests were run again.

5. Adhesion to Release Layer: Wiping Test (i.e., Peel Force Test): OPR samples which have been coated with a top release layer were cut into six 3.175 cm wide X 10.16 cm long pieces cut in the coating direction of the OPR material. Three of the
25 six pieces were mounted with silicone tape onto weighted shoes on a drum wiping mech. The release-coated surface of the samples was wiped with the carrier liquid soaked paper toweling (Kleenex Premiere brand from Kimberly Clark, Neenah, WI) for 800 rotational cycles. The paper toweling was then replaced with the carrier liquid soaked paper toweling prepared in the same manner, and the process is
30 repeated three times for a total of 3200 cycles. The three finished samples were allowed to dry overnight. Meanwhile, the three initial, unwiped samples were tested

for 180-degree peel force/adhesion using a slip/peel force tester from Instrumentors, Inc. Once the three wiped samples dried, they were also tested for peel force/adhesion in the same manner, and the results were compared to the values of the unwiped samples. All samples were tested with tape commercially available under the trade designations #202 and #600, both from Minnesota Mining and Manufacturing Company, St. Paul, MN.

Single-Layer Barrier Construction – Samples 1-16

The following tables summarize the observations taken from static crazing, electrostatic, and adhesion experiments for single layer barrier coated belts that were treated under the stated conditions.

TABLE 3

TESTING UNDER HIGH HUMIDITY CONDITIONS ($\geq 65\%$ Relative Humidity, Room Temperature)

Sample	Coating Solvent	Thickness (μm)	CTM	Crazing $\frac{1}{2}$ " bar	Crazing $\frac{1}{4}$ " bar	Electrostatics
1	DMF	0.4	50% Hydr	(m) None	(m) None	Poor
2	THF	0.4	50% Hydr	(h) Slight (l) Craze	(h) None (l) Slight	Good
3	THF/H ₂ O	0.4	50% Hydr	(l) Craze	(l) Craze	Good
4	THF/DMF	0.6	50% Hydr	(m) Heavy	(m) Heavy	Poor
5	THF	0.4	50% Hydr	(h) Craze (l) Craze	(h) Craze (l) Craze	Good
6	Water	0.5	50% Hydr	(h) Craze (l) None	(h) Craze (l) None	Good
7	Water	0.5	50% Hydr	Heavy	Medium	N/A
8	Water	0.5	50% TPD	(h) Craze (l) None	(h) Craze (l) None	OK
9	H ₂ O/MeOH	0.5	40% TPD	Slight	None	OK/Good
10	Water	0.5	50% Hydr	Medium	Light	N/A
11	MeOH/IPA	0.8	40% TPD	V. Light	V. Light	Poor
12	MeOH/IPA	0.8	40% TPD	Medium	Light	Good

13	MeOH/IP A	0.8	40% TPD	Heavy	Medium	Poor
14	MeOH/IP A	0.8	40% TPD	Heavy	Medium	Poor
15	MeOH/IP A	0.8	50% Hydr	Medium	Medium	OK
16	MeOH/IP A	0.8	50% Hydr	N/A	N/A	Poor

Humidity conditions during coating: (l) 30-40 %RH, (m) 40-50 %RH, (h) 50-65 %RH

The ideal barrier would exhibit light to no crazing on the 1/2" bar, be insensitive to the humidity during coating operation, and have good electrostatics.

5 Samples 2, 6, 8, 9, 12, and 15 show acceptable behavior at this testing stage.

In the past, constructions that were coated out of water or water / alcohol blends, for example Sample 9, crazed more severely when coated during the warmer, more humid summer months than those coated during the cooler, less humid time of the year. The temperature and relative humidity of the web coater room and the
 10 coater oven were maintained at a nearly constant setting throughout the entire year. These seasonal crazing effects have been difficult to isolate and explain, so an acrylate based terpolymer was developed that did not exhibit this type of behavior. A series of acrylate monomers were co-polymerized with itaconic acid (Samples 11 through 16) and tested in a similar fashion as the PVA based formulations.

15

TABLE 4
TESTING UNDER LOW HUMIDITY CONDITIONS ($\leq 40\%$ RH, RT)

Sample	Coating Solvent	Thickness (μm)	Crazing $\frac{1}{2}$ " bar	Crazing $\frac{3}{4}$ " bar	Electrostatics	Adhesion
1	DMF	0.4	None	None	Poor	Good
2	THF	0.4	Crazing	Slight	Good	Good
3	THF/H ₂ O	0.4	Crazing	Slight	Good	Good
4	THF/DMF	0.6	Heavy	Heavy	N/A	Good
5	THF	0.4	Crazing	Crazing	Good	Good
6	Water	0.5	None	None	OK	Poor
7	Water	0.5	Slight	None	Good	Good
8	Water	0.5	None	None	Good	Poor
9	H ₂ O/MeOH	0.5	None	None	Good	Good
10	Water	0.5	Light	None	N/A	N/A
11	MeOH/IPA	0.8	Light	None	N/A	OK
12	MeOH/IPA	0.8	Medium	Light	N/A	Poor
13	MeOH/IPA	0.8	Heavy	Light	N/A	Good
14	MeOH/IPA	0.8	Heavy	Medium	N/A	Poor
15	MeOH/IPA	0.8	Heavy	Medium	Good	Poor-Good
16	MeOH/IPA	0.8	Light	None	OK	Good

5 Samples 1 and 4 were coated using DMF as part of the solvent mixture. The barrier layer of Sample 1 provided a barrier in both high and low humidity environments but this polymer had poor electrostatics. The barrier layer of Sample 4 coated from 5 wt. % solids in (96:4) THF/DMF on Hydr CGL OPR produced a drastic change in the CGL color (from blue to a light bluish-gray color). The DMF solvent may have changed the crystalline structure of the CGL to the inactive, bluish-gray form and this could explain the poor electrostatic results. In addition, the single barrier layer in Sample 4 did not prevent crazing of the OPC.

10 The polymer used in Sample 5 is a known gas barrier, but it did not show good solvent resistance because it failed to prevent the belt from crazing at both high and low humidities.

15 Although the adhesion of the barrier layer of Sample 8 to the OPC was much better than that of Sample 6, it did not show quite as good adhesion as the barriers of Samples 1-5. Also, it failed to prevent the OPC belt from cracking at high humidity.

Dynamic crazing was another technique used to measure the extent of crazing of these single barrier layers. Those results are shown in the following table.

TABLE 5

**5 DYNAMIC CRAZING TO SIMULATE BELT FLEXIBLE FATIGUE
(40,000 cycles over a 1 inch bar at ambient room conditions)**

Sample	≤ 30 min	1 hr.	2 hr.	3 hr.	4 hr.	Appearance
10	N/A	N/A	N/A	N/A	Light	Only crazed at the edges
15	N/A	None	V. Lite	---	V. Lite	N/A
16	N/A	Lite	Lite-Med	Lite-Med	Lite-Med	N/A

Samples were tested on the dynamic crazing tester and removed periodically (after 30 min, 1, 2, 3, and 4 hr.) and visually examined for any signs of crazing.

- 10 Samples 10, 15, and 16 showed that crazing can be suppressed under cyclic fatigue conditions that are similar to those experienced during belt cycling.

Dual Barrier Layer Constructions-Examples A-

- 15 In these experiments, it was shown that the combination of the two barrier layers provides protection to the OPR from solvent across the complete range of humidity (20-80%).

- 20 In accordance with the present invention, dual barrier layer constructions were produced. In these constructions, the OPC (Hydr or TPD based) is first coated with a barrier layer coating composition that formed a barrier layer possessing good solvent resistance but is sensitive at a higher humidity to solvent-induced crazing, as demonstrated from the single-layer constructions above.

- 25 In particular, the PVA barrier layer coating compositions (Samples 6-10) and the HEMA-based barrier layer coating compositions (Examples 11-16) were coated as a first barrier layer. A second barrier layer was then coated on the first barrier layer using the barrier layer coating composition of Sample 4, having a thickness of about 0.3 μm . Finally, a top silicone release layer (0.65 μm) was coated on all of the Examples prior to testing.

TABLE 6
DUAL BARRIER TESTING UNDER LOW AND HIGH HUMIDITY
CONDITIONS

Example (undercoat Sample # + overcoat Sample #)	High Humidity (60-70 % RH, RT)			Low Humidity (30-40% RH, RT)		
	<u>Crazing</u> ½" bar	Crazing ¾" bar	Electro- statics	Crazing ½" bar	Crazing ¾" bar	Adhesion
A (6+4)	N/A	N/A	N/A	None	None	Poor
B (8+4)	None	None	N/A	None	None	Poor
C (9+4)	Medium	Light	Good	Light	None	Good
D (11+4)	V. Light	None	Poor	V. Light	None	Good
E (16+4)	N/A	N/A	N/A	Light	None	Good

5

All of the dual barrier Samples tested showed a consistent, low degree of crazing across the low and high relative humidity range. Example C showed the best crazing resistance, electrostatics, and interlayer adhesion properties of the samples evaluated.

10

Dual layer constructions including an undercoat of Sample 8, above, having a thickness within the range of about 0.3 µm and an overcoat of Sample 4 of a coating thickness of about 0.3-0.8 µm were tested under high and low humidity conditions. The following table summarizes the results.

15

TABLE 7

**STATIC CRAZING AFTER LONG TERM CONDITIONING: 70-80 %
Relative Humidity, ambient temperature**

Treatment Example (Under +Over Coat Sample #s)	19 hr.		15 days		4 months	
	½" bar	¾" bar	½" bar	¾" bar	½" bar	¾" bar
Comp. Ex. 1A (Sample 8 at 0.6 µm)	Heavy	None	Heavy	Medium	N/A	N/A
F (8+4 at 0.3 µm)	None	None	Light, Isolated	None	Light	Light
G (8+4 at 0.45 µm)	None	None	V. Light	None	Light	V. Light
H (8+4 at 0.6 µm)	None	None	Light	None	None	None

5 These results show that crazing resistance increased as the overcoat barrier layer thickness increased. Also, exposure to high humidity had very little influence on crazing (longer exposures to humidity increased the level of crazing only slightly).

10 Comparative Example 1B

A coating composition was prepared, as generally described in International Publication No. WO 95/0285 (Woo et al.). In accordance with the teachings therein, the following coating composition was prepared.

Final % in Solution	Compound
20.18	Polyvinyl Butyral (6% PVB(BX-5) in Methanol)
3.13	Colloidal silica (30% Nalco 1057 in 2,2 propoxyethanol/Water)
61.55	Isopropyl alcohol
3.07	Glycidoxypropyltrimethoxysilane (GPS) (5% GPS in 50/50 IPA/Water)
12.07	Poly(methyl vinyl ether/maleic anhydride) copolymer (1.5% GANTREZ AN-169 in Methanol/Water)

15 GPS was added to a 50:50 IPA/water solution in an amount of 5%. The resulting mixture was allowed to sit at room temperature for at least one hour. The methyl vinyl ether/maleic anhydride copolymer was added to a 75:25 methanol/water solution in an amount of 1.5% and agitated at room temperature until the solution

was clear, typically from about 1 to about 8 hours of agitation. The polyvinyl butyral was added to methanol in an amount of 6% and agitated at room temperature until the solution was clear, typically from about 1 to about 8 hours. Once these solutions were made, they were combined along with the colloidal silica and the IPA at room temperature in the amounts specified in the chart above to form a coating composition. No specific order of addition was needed.

TABLE 8
DYNAMIC CRAZING TO SIMULATE BELT FLEXURE FATIGUE (40k cycles over a 1" bar)

Construction	5 min	30 min	60 min	90 min	120 min	360 min	Appearance
Comp. Ex. 1B	Med.	Med.-Heavy	Heavy	Very Heavy	Very Heavy	N/A	Extended medium, crazing to end after 5 min
H (7+4 at 0.3 μm)	N/A	None	None	None	None	None	N/A
J (8+4 at 0.3 μm)	None	None	None	None	None	V. Light	1-2 dozen crazes/75 mm
K (8+4 at 0.45 μm)	None	None	None	None	None	None	Surface Scratches
L (8+4 at 0.6 μm)	None	None	None	None	None	None	Surface Scratches
M (9+4 at 0.3 μm)	N/A	N/A	None	None	None	None	N/A

The layer barrier construction of Example J, although much superior in performance to the bare OPC, does suffer from a slight loss in performance and shows that the overcoat should be thicker than 0.3 μm to afford protection to the OPC layers.

Electrostatic Evaluation

Dry electrostatic measurements were done to evaluate the intrinsic performance of the OPR construction without solvent. The variables under observation include charge up voltage, discharge voltage, dark decay level, extent of

ghosting during charge/discharge, and the rate of change in charge acceptance/discharge can be evaluated over 4000 revolutions of the drum.

Wet electrostatic cycling data, obtained by producing a full color print, was collected on a select group of belts. Experimental conditions are listed as an asterisk, as

5 appropriate, in Table 9.

The constructions are given as the undercoat barrier alone and then in the next row that same undercoat barrier layers with the overcoat layer barrier.

The charge acceptance voltage (Vacc), residual voltage (Vres), Dark Decay, and discharge ghost values are reported in volts after the 4,000th cycle.

10 The room temperature is reported in degrees Fahrenheit.

The change in the charge acceptance voltage (ΔV_{acc}) and the residual voltage (ΔV_{res}) are reported in volts as the difference between the 4,000th and 1st cycle values.

15 **TABLE 9**

ELECTROSTATIC CYCLING RESULTS

Construction	% RH / RT	Vacc	ΔV_{acc}	Dark Decay	Vres	ΔV_{res}	Discharge Ghost
6 ¹	27/72	845	45	31	123	68	23
N (6+4)	30/72	850	40	30	150	75	25
7	N/A	N/A	N/A	N/A	N/A	N/A	N/A
O (7+4)	18/77	785	5	60	120	50	15
8	19/73	860	30	60	70	10	15
P (8+4)	66/78	724	-2	64	60	7	15
9	59/81	728	-1	76	64	9	6
Q (9+4)	54/81	753	-2	49	71	5	33
11	74/77	475	-185	110	70	0	5
R (11+4)	74/77	540	-120	140	95	35	10
12 ²	71/78	660	-15	90	80	-30	20
S ² (12+4)	71/78	650	-30	90	60	-45	25
13	75/77	400	-170	125	70	-5	0
T (13+4)	75/77	560	-120	120	125	-25	15
14	75/77	520	-55	145	80	-10	10
U (14+4)	75/77	605	-50	155	140	0	20

¹Leveled off after 1400 cycles, no release

²Leveled off after 200 cycles

The preferred charge acceptance voltage is above 550 V and a value that changes by less than 55 volts over 4,000 cycles. A low residual voltage is desired, preferably below 125 volts, with less than a 50 volt change over 4,000 cycles. A dark decay voltage of less than 65 volts and discharge ghost voltage of less than 35
5 volts are desirable.

Most of the constructions given in Table 9 have several of the desirable dry electrostatic properties, although some do not meet all of the standards at this time. Improvements in the coating quality and purity levels of the barrier binders are expected to improve the electrostatic response.

10 The latter constructions (those involving the HEMA type barriers) were evaluated at high humidity levels, which explains why some of the electrostatic results were outside of the desirable levels.

All patents, patent applications, and publications disclosed herein are incorporated by reference in their entirety, as if individually incorporated. The
15 foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims.

What is claimed is:

1. An organic photoreceptor comprising:
 - an organic photoconductor having a first major surface and a second major surface;
 - 5 a barrier layer comprising:
 - an undercoat formed on the first major surface of the photoconductor from an undercoating composition comprising a poly(vinyl alcohol), a methylvinylolether/maleic anhydride copolymer, and a crosslinker; and
 - 10 an overcoat formed on the undercoat from an overcoating composition comprising a material selected from the group consisting of an amine-containing hydroxyether, an amide-containing hydroxyether, and a combination thereof; and
 - a release layer.
- 15 2. The organic photoreceptor of claim 1, wherein at least one of the undercoating composition and the overcoating composition further comprises an optional additive.
- 20 3. The organic photoreceptor of claim 1, wherein the barrier layer has a thickness of about 0.5 micrometers to about 1.3 micrometers.
4. The organic photoreceptor of claim 7, wherein the undercoat has a thickness of about 0.2 micrometers to about 0.5 micrometers.
- 25 5. The organic photoreceptor of claim 7, wherein the overcoat has a thickness of about 0.3 micrometers to about 0.8 micrometers.
6. The organic photoreceptor of claim 1, wherein the organic photoreceptor is
30 in a form of a flexible belt.

7. The organic photoreceptor of claim 1, further comprising a tie layer, wherein the tie layer is positioned on the overcoat layer of the barrier layer.

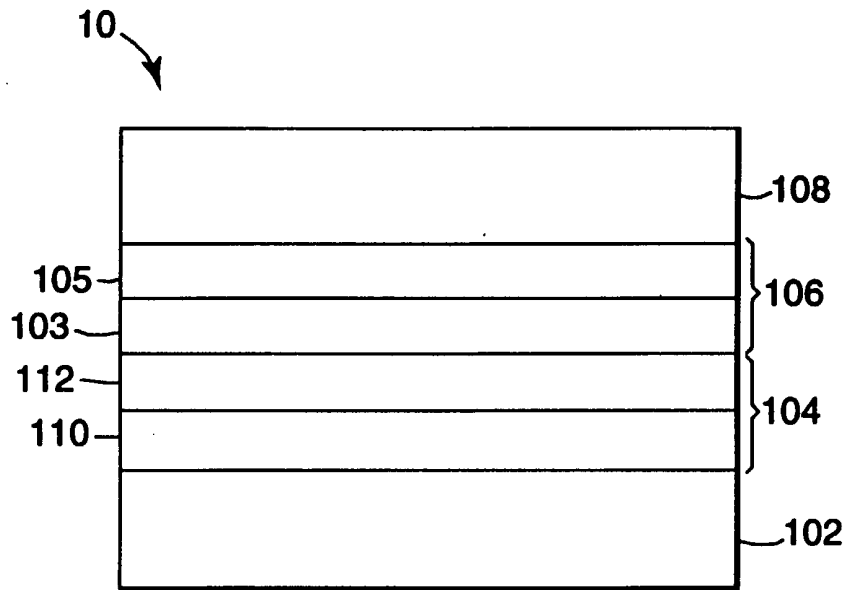


Fig. 1a

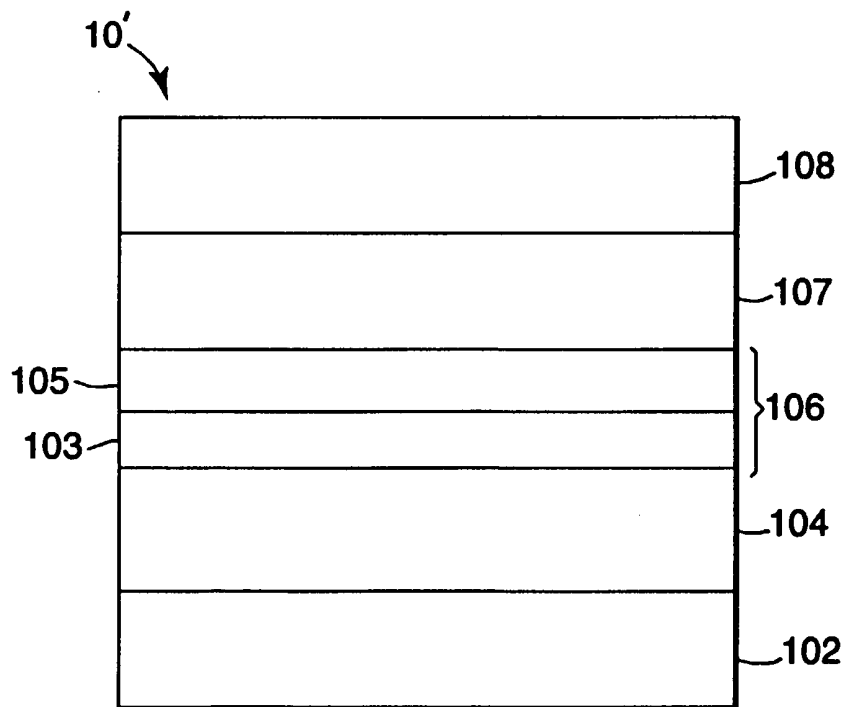


Fig. 1b

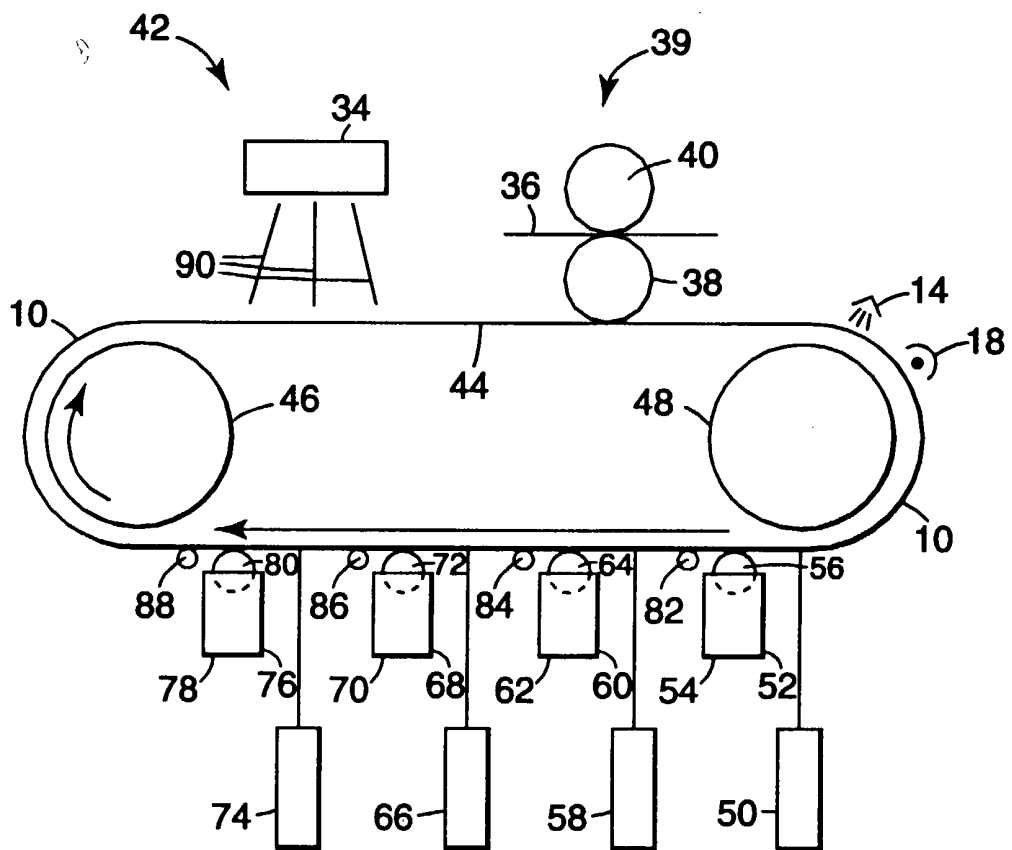


Fig. 2

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US 01/40396

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 G03G5/147 G03G5/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 G03G C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 02853 A (MINNESOTA MINING & MFG) 26 January 1995 (1995-01-26) page 22; examples 12-17; table 1 claim 1	1-7
A	US 5 756 246 A (ENDER DAVID A ET AL) 26 May 1998 (1998-05-26) column 8; tables 1,2 claims 1,2	1-7
A	US 5 464 924 A (SILVIS H CRAIG ET AL) 7 November 1995 (1995-11-07) column 7 -column 8; figure 1	1

 Further documents are listed in the continuation of box C.

 Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- * & * document member of the same patent family

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INTERNATIONAL SEARCH REPORT
 Information on patent family members

International Application No
 PCT/US 01/40396

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9502853 A	26-01-1995	US 6001522 A DE 69416843 D DE 69416843 T EP 0719426 A JP 9500222 T	14-12-1999 08-04-1999 11-11-1999 03-07-1996 07-01-1997
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