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(54) Electrophotographic imaging member.

(57) An electrophotographic imaging member containing a supporting substrate having an electrically conductive surface, a charge blocking layer including a vinyl hydroxy ester or vinyl hydroxy amide polymer and at least one photoconductive layer, the charge blocking layer having a surface resistivity greater than about 10^{10} ohm/sq. This imaging member may be employed in an electrostatographic imaging process.

ELECTROPHOTOGRAPHIC IMAGING MEMBER

BACKGROUND OF THE INVENTION

This invention relates in general to electrostatography and, more specifically, to a novel photoconductive device and process for using the device.

In the art of xerography, a xerographic plate containing a photoconductive insulating layer is imaged by first uniformly electrostatically charging its surface. The plate is then exposed to a pattern of activating electromagnetic radiation which selectively dissipates the charge in the illuminated areas of the photoconductive insulator while leaving behind an electrostatic charge pattern in the nonilluminated areas. This resulting electrostatic latent image may then be developed to form a visible image by depositing finely divided electroscopic marking particles on the surface of the photoconductive insulating layer.

A photoconductive layer for use in xerography may be a homogeneous layer of a single material such as vitreous selenium or it may be a composite layer containing a photoconductor and another material. One type of composite photoconductive layer used in xerography is illustrated in US-A 4,265,990 which describes a photosensitive member having at least two electrically operative layers. One layer comprises a photoconductive layer which is capable of photogenerating holes and injecting the photogenerated holes into a contiguous charge transport layer. Generally, where the two electrically operative layers are supported on a conductive layer with the photoconductive layer sandwiched between the contiguous charge transport layer and a supporting conductive layer, the outer surface of the charge transport layer is normally charged with a uniform charge of a negative polarity and the supporting electrode is utilized as an anode. Obviously, the supporting electrode may also function as an anode when the charge transport layer is sandwiched between the anode and a photoconductive layer which is capable of photogenerating electrons and injecting the photogenerated electrons into the charge transport layer. The charge transport layer in this embodiment, of course, must be capable of supporting the injection of photogenerated electrons from the photoconductive layer and transporting the electrons through the charge transport layer.

Various combinations of materials for charge generating layers (CGL) and charge transport layers (CTL) have been investigated. For example, the photosensitive member described in US-A 4,265,990 utilizes a charge generating layer in contiguous contact with a charge transport layer comprising a polycarbonate resin and one or more of certain diamine compounds. Various generating layers comprising photoconductive layers exhibiting the capability of photogeneration of holes and injection of the holes into a charge transport layer have also been investigated. Typical photoconductive materials utilized in the generating layer include amorphous selenium, trigonal selenium, and selenium alloys such as selenium-tellurium, selenium-tellurium-arsenic, selenium-arsenic, and mixtures thereof. The charge generation layer may comprise a homogeneous photoconductive material or particulate photoconductive material dispersed in a binder. Other examples of homogeneous and binder charge generation layer are disclosed, for example, in US-A 4,265,990. Additional examples of binder materials such as poly(hydroxyether) resins are taught in US-A 4,439,507. The disclosures of the aforesaid US-A Patent 4,265,990 and US-A 4,439,507 are incorporated herein in their entirety. Photosensitive members having at least two electrically operative layers as disclosed above provide excellent images when charged with a uniform negative electrostatic charge, exposed to a light image and thereafter developed with finely divided electroscopic marking particles. However, when the supporting conductive substrate comprises a charge injecting metal or non-metal, difficulties have been encountered with these photosensitive members due to discharge in the dark. More specifically, these photosensitive members do not retain sufficient charge during the charging and subsequent imaging exposure and development steps. Most metallic ground planes have a natural oxide layer which inhibits charge injection. Typical metals of this type are aluminum, zirconium, titanium and the like. Some exceptions are metals that do not oxidize such as the noble metals, e.g., gold, platinum and the like that promote charge injection. Ground planes containing other materials such as copper iodide or carbon black also inject charge into charge generation layers so the photoreceptor does not effectively hold charge during the charging, image exposure and/or development steps. Copper iodide ground planes as disclosed in, for example, US-A 4,082,551 encounter degradation problems during cycling. Charge blocking layers are frequently used on metalized or other kinds of ground planes to inhibit charge injection. Some charge blocking layers require an additional adhesive layer between the charge generation layer and the conductive ground plane. When attempts are made to use resins as a blocking layer, the photoreceptors usually exhibit increased residual charge with cycling. Failure to effectively hold charge during the image exposure and development steps or increased residual charge formation with cycling cannot normally be tolerated in precision copiers, duplicators, and printers.

Copolymers of methyl vinyl ether and maleic anhydride such as the Gantrez AN resins from GAF Corporation have been utilized in blocking layers. Unfortunately, these copolymers of methyl vinyl ether and maleic anhydride are sensitive to water and rapidly hydrolyze to form acidic products which are corrosive and attack metal ground planes of photoreceptors during electrical cycling. Loss of the ground plane due to corrosion during electrical cycling eventually prevents an electrophotographic imaging member from discharging. This is manifested by an increase in background toner deposits in the final image during electrical cycling. In addition, the mechanical properties of copolymers of methyl vinyl ether and maleic anhydride are affected at high humidity and cause flexible electrophotographic imaging members to delaminate. Under low humidity conditions, blocking layers containing copolymers of methyl vinyl ether and maleic anhydride tend to cause electrical surface potential cycle down. Cycle down affects the final copy by causing loss of electrical contrast between exposed and unexposed areas. In addition, copolymers of methyl vinyl ether and maleic anhydride are sensitive to certain solvents utilized in subsequently applied layers and redissolve and lose integrity as a blocking layer. Hydrolysis of copolymers of methyl vinyl ether and maleic anhydride transforms the anhydride to the acid. The acid formed during storage will attack the metallic conductive layer and result in photoreceptors that will no longer discharge. Moreover, during cycling, corrosion of thin metal ground planes is accelerated and this will also result in photoreceptors that will no longer discharge. Also, when the acid is formed, coating with the material is generally restricted to coating with water and low molecular weight alcohols.

Poly(vinylalcohol) (PVOH) has been evaluated for use as a blocking layer. However, this material is very viscous and difficult to apply as a coating. For example, very dilute but still viscous poly(vinylalcohol) aqueous solutions requires numerous spray coating passes to build up blocking layer dry thickness to the desired level. Moreover, the solvents that may be employed for poly(vinylalcohol) are not conducive to the formation of high quality coatings. In addition, the adhesion of poly(vinylalcohol) to many conductive layer polymers is poor.

INFORMATION DISCLOSURE STATEMENT

US-A 3,932,179 issued to E. A. Perez-Albuerne on January 13, 1976 - A multilayer electrophotographic element is disclosed comprising a conducting layer, a photoconductive layer, and a polymeric interlayer having a surface resistivity greater than about 10^{12} ohm/sq between the conducting layer and the photoconductive layer. The interlayer comprises a blend of at least two distinct polymeric phases comprising: (a) a film forming water or alkali-water soluble polymer and (b) an electrically insulating, film forming, hydrophobic polymer. For example, the conducting layer may contain cuprous iodide imbibed in a copolymeric binder of polymethylmethacrylate and polymethacrylic acid. A complex two phase hazy layer, composed of a complex terpolymer (65 wt. percent) of poly-(methylacrylate-vinylidene chloride-itaconic acid) and polyvinylmethylether maleic anhydride) (35 wt. percent) is employed as an organic solvent barrier, an adhesive aid, and a hole blocking layer. The film forming water or alkali-water soluble polymer may contain pendant side chains composed of groups such as acidic, hydroxy, alkoxy and ester groups.

US-A 4,082,551 issued to Steklenski et al on April 4, 1978 - A unitary photoconductive element is disclosed having an electrically conducting layer, a photoconductive layer thereon, and a multilayer interlayer composition interposed between the conducting layer and the photoconductive layer. The multilayer interlayer composition comprises a layer containing an acidic polymer material, a layer containing a basic polymer material, and an acid-base reaction product zone formed at the interface of the acidic polymer-containing layer and the basic polymer-containing layer. The basic polymer materials appear to be basic because of the presence of amine groups. Various basic amino methacrylate and acrylate monomers and polymers are disclosed. Thus, for example, the complex barrier bilayer adjacent to a CuI conductive layer may be composed of an acrylic or methacrylic acid copolymer and the top layer composed of a poly 2-vinylpyridine-polymethylmethacrylate copolymer such that a salt interlayer forms at the interface of these acidic and basic polymers. The multilayer interlayer composition provides good adhesion between the conducting and photoconductive layers of the resultant unitary element and can function as an electrical barrier blocking positive charge carriers which might otherwise be injected into the photoconductive layer from the underlying conducting layer.

US-A 4,584,253 issued to Lin et al on April 22, 1986 - An electrophotographic imaging member is disclosed comprising a charge generation layer, a contiguous charge transport layer and a cellulosic hole trapping material located on the same side of the charge transport layer as the charge generation layer. In one example, the cellulosic hole trapping material may be sandwiched between the charge generation layer and an electrically conductive layer.

US-A 3,113,022 issued to P. Cassiers et al on December 3, 1963 - An electrophotographic imaging member for forming latent conductivity images is disclosed. The conductive layer for the member may include gold and various other materials such as a hydrophilic material comprising a hygroscopic and/or antistatic compound and a hydrophilic binding agent. Suitable hygroscopic and/or antistatic compounds include, for example, glycerine, glycol, polyethylene glycols, hydroxypropyl sucrosemonolaurate, etc. Suitable hydrophilic binding agents include gelatin, polyvinyl alcohol, methylcellulose, carboxymethylcellulose, cellulosesulphate, cellulose hydrogen phthalate, cellulose-acetatesulphate, hydroxyethyl cellulose, etc. for obtaining a good adhesion of a hydrophilic layer and a hydrophobic polymeric sheet. Also, a coating of a polymeric substance may be used on paper sheets to prevent organic polymeric photoconductive substance and radiation sensitive substance from penetrating within the paper sheet. The coating of a polymeric substance must not prevent the carrying off of electrons from exposed image areas during radiation. Coatings include cellulose diacetate, cellulose triacetate, cellulose acetobutyrate, ethyl cellulose, ethyl cellulose stearate or other cellulose derivatives, polymerisates such as polyacrylic acid esters, polymethacrylic acid esters, polycondensates such as polyethylene glycol esters, diethylene glycol polyesters, etc. An organic polymeric photoconductive substance together with a radiation-sensitive substance is dissolved or dispersed in an organic solvent and coated onto the surface of a suitable support.

US-A 3,245,833 issued to D. Trevoy on April 12, 1966 - Electrically conductive coatings useful as antistatic coatings on photographic films are prepared from cuprous iodide and organic polymers in nitrile solvents (e.g. Example 6). Surface resistivities of 7-9 x 10^3 ohms/square were obtained after spin coating and drying. Thicknesses do not appear to be disclosed. Coating applications do not appear to be electrophotographic and a polymeric insulative binder is always used with the cuprous iodide wherein the semiconductor metal containing compound (CuI) is present in the 15-90 volume percent range.

US-A 3,428,451 issued to D. Trevoy - Appears to employ some of the conductive coatings described in US-A 3,245,833 (see above) for use in electrically conductive supports for radiation sensitive recording elements (e.g. an electron microscope where direct electron recording is carried out). Coating applications do not appear to be electrophotographic.

US-A 3,554,742 issued to - Conductive coatings (e.g. CuI and polymeric binder) described in US-A 3,245,833 (see above) appear to be employed in electrophotographic applications. A binder is used with the cuprous iodide as the conductive layer. Barrier layers of block copolycarbonates located between the conductive layer (CuI and polymeric binder) and a photoconductive layer (e.g thiapyrilium) improve adhesion to each and charging levels. However, no cyclic electrical data is provided.

US-A 3,640,708 issued to W. D. Humphries et al - A mixture of CuI and polymeric binder is employed as a conductive layer for electrophotographic devices. Barrier layers, located as described in reference (3), of a polymeric blend of cellulose nitrate and a complex tetrapolymer of methyl acrylate, acrylonitrile, acrylic acid and vinylidene chloride having a thickness of 0.3 to 0.5 micrometer were found to reduce dark decay and improve adhesion. No cyclic electrical data is provided.

US-A 3,745,005 issued to W. E. Yoerger et al - A mixture of cuprous iodide in a polymeric binder (polyvinylformal) is employed as a conductive layer. A barrier layer (0.3 - 7 micrometers) consists of a copolymer of vinylacetate and vinylpyrrolidone or vinylacetate and an $\alpha\beta$-unsaturated monoalkenoic acid gives charging levels in the range of 600 to 700 volts in an RH range of 15-80 percent. Claims 3 and 7 refer to conductive layers of carbon dispersed in a binder although this kind of conductive layer is not discussed elsewhere in this patent. No cyclic electrical data is provided.

US-A 4,485,161 issued to M. Scozzafava et al - Conductive layers containing cuprous iodide in the polymeric binders are disclosed. Barrier layers were solution or bulk coated from polymerizable and crosslinkable monomers having at least one acrylate or methacrylate group and also having an aromatic nucleus or cycloaliphatic nucleus. The barrier layer coating also contained small amounts of a photosensitizer and an amine activator required to promote UV radiation cure of the neat monomer coating. Dry barrier layer coating thicknesses of 2-8 micrometers were obtained. These devices were capable of supporting electric fields of 1.3 to 1.6 x 10^6 volts/cm under corona charging. The $E\frac{1}{2}$ photosensitivity was about 10 ergs/cm^2 (Example 3) of 640 nm incident light. The $E\frac{1}{3}$ photosensitivity (Examples 2,4,5 and 6) ranged from 6.7-14.9 ergs/cm^2 using the same light source. No test of a barrier layer V_O and V_R behavior with repeated xerographic cycling is given. The above data is for only one cycle. These crosslinked barrier layers do reduce the number of white spots produced in the imaged film. The barrier layer also functions as a solvent barrier to toluene and methylene chloride in addition to its electrical function as a hole injection barrier.

US-A 4,465,751 issued to K. Kawamura et al - The formation of cuprous iodide conductive layers are disclosed wherein the cuprous iodide is imbibed into the polymeric substrate or a subbing adhesive layer on the polymeric substrate when the cuprous iodide - acetonitrile solution is coated without a binder in the same solution. Thus, a binder for the cuprous iodide is generated underneath the CuI by appropriate solvent swelling and/or heat and the result is a CuI - binder conductive layer. Optionally, a CuI - polymer conductive layer wherein cellulose acetate butyrate is used as the polymeric binder is coated directly. The CuI is imbibed and no distinct CuI layer remains.

US-A 4,410,614 issued to Lelental et al on October 18, 1983 - An electrically activatable recording element is disclosed comprising a polymeric electrically active conductive layer. A list of useful copolymers for the polymeric electrically active conductive layer includes many polymethacrylates can be found at column 6, lines 36-62. Synthetic polymers are preferred as vehicles and binding agents in the layers of the electrically activatable recording element. The use of polymers such as poly(vinylpyrrolidone), polystyrene and poly(vinylalcohol) is disclosed at column 11, lines 14-58.

US-A 4,262,053 issued to Burwasser on April 14, 1981 - An antiblocking agent for dielectric film for electrostatographic recording is disclosed. The dielectric imaging element may comprise a dielectric film, a film support and conductive layers. The conductive layers include polymers such as quaternized polymers of vinylpyridine with aliphatic esters, polymers of polyacrylic acid salts with metallic coated polyester films, and the like. The conductive layers may be coated with various dielectric resins including styrenated acrylics.

Koji Abe, Mikio-Koide and Eishum Tcuchida, Macromolecules 10 (6), 1259-64 (1977) - A polymeric complex is prepared from 4-vinylpyridine (a basic polymer) and polymethyl acrylic acid (an acidic polymer) to vie a significant amount of the ionized salt structure (Figure III).

M.M. Coleman and D.J. Skrovanek, Conference Proceeding of 44th ANTEC, 321-2 (1986) - Poly-2-vinylpyridine is shown to interrupt routine hydrogen bonding in an amorphous neutral nylon polymer. The neutral polymer provides an amide hydrogen as a hydrogen bonding site.

US-A 3,295,967 issued to S. J. Schoenfeld on January 3, 1967 - An electrophotographic recording member is disclosed which contains a non-metallic base of high electrical resistivity, a coating on the base for increasing the electrical conductivity, the coating comprising gelatinous hydrated silicic acid and a hygroscopic hydrated inorganic salt, and a photoconductive stratum covering the coating.

US-A 4,464,450 issued to L. A. Teuscher on August 7, 1984 - an electrostatographic imaging member is disclosed having electrically operative layers overlying a siloxane film coated on a metal oxide layer of a metal conductive anode, the siloxane having reactive OH and ammonium groups attached to silicon atoms.

U.K. Patent Application GB 2 009 600 A to Tadaju Fukuda et al, published April 23, 1982 - A photoconductive member is disclosed comprising a support, a photoconductive layer constituted of an amorphous material comprising silicon atoms as a matrix and a barrier layer between the support and the photoconductive layer, the barrier layer comprising a first sub-layer constituted of an amorphous material comprising silicon atoms as a matrix and containing an impurity which controls the conductivity and a second sub-layer constituted of an electrically insulating material different from the amorphous material constituting the first sub-layer.

Thus, the characteristics of photosensitive members comprising a support having an electrically conductive charge injecting surface, a blocking layer and at least one photoconductive layer, exhibit deficiencies as electrophotographic imaging members.

SUMMARY OF THE INVENTION

It is an object of the invention to provide an electrophotographic imaging member which overcomes the above-noted disadvantages.

It is an another object of this invention to provide an electrostatographic imaging member having extend life.

It is another object of this invention to provide an electrostatographic imaging member that charges to high voltages useful in xerography.

It is another object of this invention to provide an electrostatographic imaging member which is more dark stable.

It is another object of this invention to provide an electrostatographic imaging member which allows photodischarge with low residual voltage during cycling under most ambient relative humidities.

It is another object of the invention to provide an electrostatographic imaging member that is simpler to fabricate.

It is another object of the invention to provide an electrostatographic imaging member having a blocking layer that is resistant to disturbance or dissolving by components of subsequently applied layers.

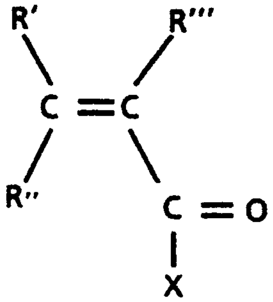
These and other objects of the present invention are accomplished by providing an electrophotographic imaging member comprising a supporting substrate having an electrically conductive surface, a charge blocking layer comprising a vinyl hydroxy ester or vinyl hydroxy amide polymer and at least one photoconductive layer, the charge blocking layer having a surface resistivity greater than about 10^{10} ohm/sq. This imaging member may be employed in an electrostatographic imaging process.

The supporting substrate layer having an electrically conductive surface may comprise any suitable rigid or flexible member such as a flexible web or sheet. The supporting substrate layer having an electrically conductive surface, may be opaque or substantially transparent, and may comprise numerous suitable materials having the required mechanical properties. For example, it may comprise an underlying insulating support layer coated with a thin flexible electrically conductive layer, or merely a conductive layer having sufficient internal strength to support the electrophotoconductive layer. Thus, the electrically conductive layer may comprise the entire supporting substrate layer or merely be present as a component of the supporting substrate layer, for example, as a thin flexible coating on an underlying flexible support member.

The electrically conductive layer may comprise any suitable electrically conductive organic or inorganic material. Typical electrically conductive layers including, for example, aluminum, titanium, nickel, chromium, brass, gold, stainless steel, carbon black, graphite, metalloids, cuprous iodide, indium tin oxide alloys, Lewis acid doped polypyrrole and the like. The electrically conductive layer may be homogeneous or heterogeneous, e.g. conductive particles dispersed in a film forming binder. When hole injecting materials such as carbon black, copper iodide, gold and other noble metals, platinum, polypyrrole, polyaromatic conducting polymers, polythiothenes, conducting metallic oxide such as antimony tin oxide, indium tin oxide, and the like are utilized in a conductive layer, photoreceptors that do not contain a suitable blocking layer can often discharge in the dark thereby rendering the photoreceptor unsuitable for electrophotographic imaging. The ground plane should be continuous and at least monomolecular in thickness. The continuous conductive layer may vary in thickness over substantially wide ranges depending on the desired use of the electrophotoconductive member. Accordingly, the conductive layer can generally range, for example, in thicknesses of from about 50 Angstrom units for some materials to many centimeters. For some ground planes, such as those containing carbon black, a minimum thickness of about 0.5 micrometer is preferred. When a highly flexible photoresponsive imaging device is desired, the thickness of conductive layers may be between about 100 Angstroms to about 2,000 Angstroms. The resistivity of the ground plane should be less than about 10^8 and more preferably 10^6 ohms/square for efficient photoreceptor discharge during repeated cycling. If an underlying flexible support layer is employed, it may be of any conventional material including metal, plastics and the like. Typical underlying flexible support layers include insulating or non-conducting materials comprising various resins or mixtures thereof with conductive particles, such as metals, carbon black and the like, known for this purpose including, for example, polyesters, polycarbonates, polyamides, polyurethanes, and the like. The coated or uncoated supporting substrate layer having an electrically conductive surface may be rigid or flexible and may have any number of different configurations such as, for example, a sheet, a cylinder, a scroll, an endless flexible belt, and the like. Preferably, the flexible supporting substrate layer having an electrically conductive surface comprises an endless flexible belt of commercially available polyethylene terephthalate polyester coated with a thin flexible metal coating. Generally, the material selected for the ground plane should not be attacked by solvents ultimately selected for use with the subsequently applied blocking layer. If the blocking layer solvent attacks the ground plane, it may leach out and/or physically dislodge hole injecting components from the ground plane into the blocking layer. In subsequent coating operations, these already migrated hole injection components in the blocking layer may further migrate into the charge generating layer or charge transporting layer from which dark discharge and low charge acceptance can occur. Since hole injection in the charge generating layer or charge transporting layer is cumulative with xerographic cycling, V_0 also decreases with cycling (V_0 cycle-down).

A charge blocking layer is interposed between the conductive surface and the imaging layer. The imaging layer comprises at least one photoconductive layer. This blocking layer material traps positive charges. The charge blocking layer of this invention comprises a uniform, continuous, coherent blocking layer comprising a vinyl hydroxy ester or vinyl hydroxy amide polymer.

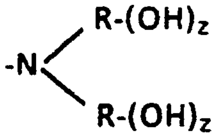
The vinyl hydroxy ester or vinyl hydroxy amide polymer of the blocking layer of this invention is preferably a polymeric reaction product involving at least a vinyl hydroxy ester or vinyl hydroxy amide monomer having the following structure:



wherein
X is selected from the group consisting of:

$-O-R-(OH)_z$, $-NH-R-(OH)_z$

$-NR-R-(OH)_z$ and



R
is a divalent group selected from the group consisting of aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms;
z
contains from 1 to 10 hydroxyl groups; and
R',R'' and R'''
are monovalent groups independently selected from the group consisting of hydrogen, aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms.

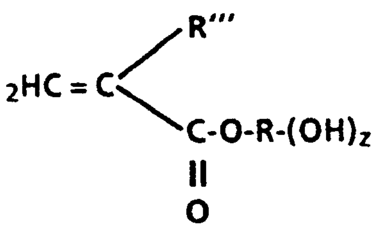
Typical divalent R aliphatic groups include methylene, ethylidene, propylidene, isopropylidene, butylene, isobutylene, decamethylene, phenylene, biphenylene, piperadinylene, tetrahydrofuranylene, pyranylene, piperazinylene, pyridylene, bipyridylene, pyridazinylene, pyrimidinylene, naphthylidene, quinolinyldene, cyclohexylene, cyclopentylene, cyclobutylene, cycloheptylene, and the like.

Typical monovalent R', R'' and R''' groups include hydrogen, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, decyl, phenyl, biphenyl, piperadinyl, tetrahydrofuranyl, pyranyl, piperazinyl, pyridyl, bipyridyl, pyridazinyl, naphthyl, quinolinyl, cyclohexyl, cyclopentyl, cyclobutyl, cycloheptyl, and the like.

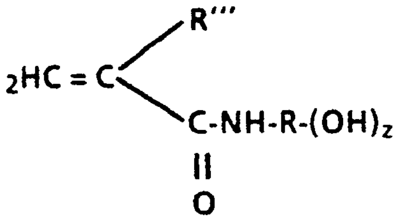
Typical aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms include linear, single ring and multiple ring, fused and unfused groups such as napthalene, thiophene, quinoline, pyridine, furan, pyrrole, isoquinoline, benzene, pyrazine, pyrimidine, bipyridine, pyridazine, and the like.

The polymeric reaction product of a vinyl hydroxy ester or vinyl hydroxy amide monomer having the above structure may be a homopolymer or copolymer. The copolymer may be a copolymer of 2 or more different monomers or polymer blocks.

Examples of preferred embodiments of monomers having the above structure include those having the following structures:



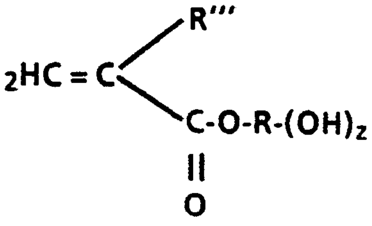
and



wherein:

R	is a lower aliphatic group containing from 1 to 5 carbon atoms,
R'''	is CH_3 or hydrogen, and
z	is 1 to 5.

Optimum results are achieved with monomers having the above structure include those having the following structure:

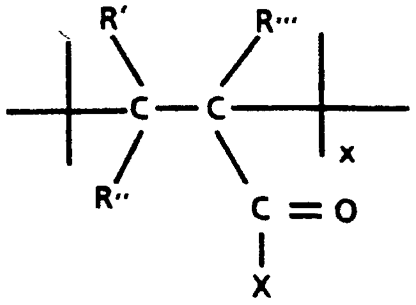


wherein:

R	is a lower aliphatic group containing from 2 to 3 carbon atoms,
R'''	is CH_3 or hydrogen, and
z	is 1 or 2.

These monomers can be prepared to yield compositions having a high degree of purity without electrically deleterious catalyst and/or monomer residuals, and at very high weight average molecular weights (e.g. ≧ 1,000,000). Moreover, these polymers are soluble in lower alcohols having from 1 to 4 carbon atoms which enables the coating of these materials on top of organic or inorganic (generally alcohol insoluble) conductive layers without washing away the conductive layer with the alcohol coating solvent. In addition, because these polymers are alcohol soluble and have minimal solubility in more organic coating solvents (such as toluene, tetrahydrofuran, and chlorinated alkanes), subsequently used organic coating compositions overcoated onto the blocking layer do not erode away the blocking layer. If erosion were to occur, the thin or shallow blocking layer areas would cause high dark decay and low charge acceptance.

The vinyl hydroxy ester or vinyl hydroxy amide polymer may be a homopolymer, a copolymer, a terpolymer or the the like. A preferred homopolymer is represented by the following formula:



wherein:

x

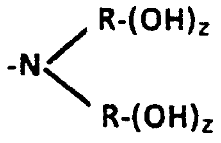
represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000,

X

is selected from the group consisting of groups represented by the following groups:

$-O-R-(OH)_z$, $-NH-R-(OH)_z$

$-NR-R-(OH)_z$ and



$-N(R-(OH)_z)_2$

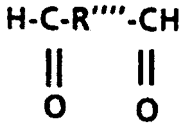
R
is selected from the group consisting of aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms;
z
contains from 1 to 10 hydroxyl groups; and
R', R'' and R'''
are independently selected from the group consisting of hydrogen, aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms.

Typical vinyl hydroxy ester polymers and vinyl hydroxy amide polymers include poly(4-hydroxybutyl)-methacrylate, poly(4-hydroxybutyl)acrylate, poly(3-hydroxypropyl)methacrylate, poly(3-hydroxypropyl)-acrylate, poly(2,3-dihydroxypropyl)methacrylate, poly(2,3-dihydroxypropyl)acrylate,poly(2,3,4-trihydroxybutyl)methacrylate, poly(2,3,4-trihydroxybutyl)acrylate, poly(N-2,3 dihydroxypropyl)methacrylamide, poly-(N-2,3 dihydroxypropyl)acrylamide, poly(N-hydroxymethyl)methacrylamide, poly(N-hydroxymethyl)-acrylamide, poly(N-2-hydroxyethyl)methacrylamide, poly(N-2-hydroxyethyl)acrylamide, poly(4-hydroxyphenyl)methacrylate, poly(4-hydroxyphenyl)acrylate, poly(3-hydroxyphenyl)methacrylate, poly(3-hydroxyphenyl)acrylate, poly(N-3 or 4-hydroxyphenyl)methacrylamide, poly(N-3 or 4-hydroxyphenyl)acrylamide, poly[4(2-hydroxypyridyl]methacrylate, poly[4(2-hydroxypyridyl]acrylate, poly[4(3-hydroxypiperidinyl]-methacrylate, poly[4(3-hydroxypiperidinyl]acrylate, poly[N-4(2-hydroxypyridyl]methacrylamide, poly[N-4(2-hydroxypyridyl]acrylamide, poly[N-4(3-hydroxypiperindinyl]methacrylamide, poly[N-4(3-hydroxypiperindinyl]acrylamide, poly[1(5-hydroxynaphthyl]methacrylate, poly[1(5-hydroxynaphthyl]acrylate, poly[N-1(5-hydroxyethylnaphthyl]methacrylamide, poly[N-1(5-hydroxyethylnaphthyl]acrylamide, poly[1(4-hydroxycyclohexyl]methacrylate, poly[1(4-hydroxycyclohexyl]acrylate, poly[N-1(3-hydroxycyclohexyl]-methacrylamide, poly[N-1(3-hydroxycyclohexyl]acrylamide, and the like.

Poly(2-hydroxyethylmethacrylate) [P(HEMA)] and poly(2-hydroxyethylacrylate) [P(HEA)] are particularly insoluble in subsequently employed organic coating solvent. P(HPMA) and P(HPA) exhibit some solubility in tetrahydrofuran when stirred in that solvent at room temperature for a prolonged time period (overnight). If the solvent evaporation is rapid, such as in a coating process normally employed to manufacture photoreceptors, then tetrahydrofuran solubility of the blocking layer polymer is an unlikely problem. Further, these polymers, particularly P(HEMA), attract about one weight percent water and retain much of the trapped water in a dense hydrogen bonding network even at low RH. The trapped water assists in the transport of photodischarged electrons through the blocking layer to the conductive layer and also assists in preventing electron trapping and V_R cycle-up. The higher the hydroxyester or hydroxyamide blocking layer polymer molecular weight, the higher the intermolecular H-bonding density, the trapping of water and the solvent barrier (to prevent solvent wash away of the blocking layer) properties of these polymers.

The presence of the ester group or amide group along with a hydroxyl group in each polymeric repeat unit not only maximizes intermolecular H-bonding in the form of OH-OH H-bonding and carbonyl (of the ester or amide) -OH-bonding, but also allows for some intramolecular (5,6 and 7 membered rings) H-bonding to maintain overall H-bonding density particularly in those blocking layer areas where intermolecular H-bonding is below the average, presumably because of conformationally unfavorable chain configurations. Thus, this intramolecular mode of H-bonding along with trapped water can maintain high H-bonding density which assists electron transport and completes photodischarge (low V_R). All of these properties contribute to enhanced photoreceptor electrical performance.

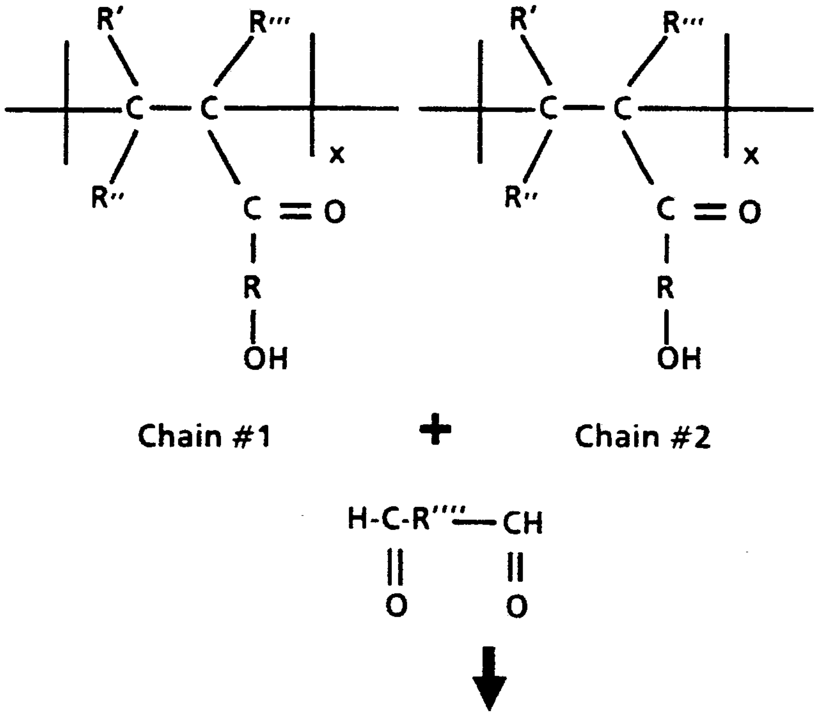
The vinyl hydroxy ester or vinyl hydroxy amide polymer may be crosslinked and uncrosslinked. If crosslinked, crosslinking may be effected by any suitable difunctional (or higher polyfunctionality) compound (usually a small molecule) that can react with hydroxyl groups at temperatures of less than about 135° C (where the substrate is polyethylene terephthalate) may be employed to crosslink the hydroxy ester or hydroxy amide polymers through the hydroxyl groups. Higher temperatures may be utilized if the substrate is not adversely softened at the reaction temperatures. Typical polyfunctionality compounds include diisocyanates such as toulenediisocyanate, methylenediisocyanate, isophoronediisocyanate, hexamethylenediisocyanate, and the like, blocked diisocyanates, polyfunctional aziridines such as XAMA-2 and the like, and polyfunctional epoxides such as 1,3-butadienediepoxide, 1,4-butanediol diglycidyl ether, ethylene glycol diglycidyl ether, neopentyl glycol diglycidyl ether, bisphenol A diglycidyl ether, 1,4-divinylbenzene diepoxide, difunctional aldehydes and the like. The difunctional aldehyde may having the following structure:



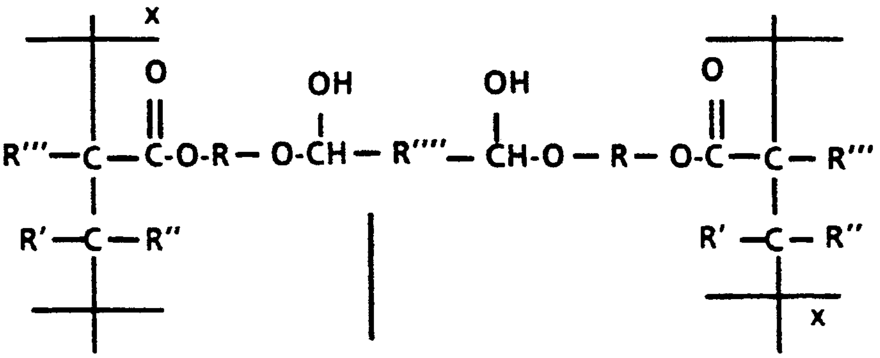
$$\mathrm{H-\underset{\underset{O}{\|}}{C}-R''''-\underset{\underset{O}{\|}}{C}H}$$

wherein R'''' is a divalent hydrocarbon or heteroaromatic unit or covalent bond. Typical R'''' groups include methylene, ethylene, propylene, phenylene, biphenylene, pyridylene, and the like. Typical difunctional aldehydes include, for example, glutaraldehyde, glyoxal, 2,6-pyridinedicarboxaldehydes, terephthalaldehyde, and the like.

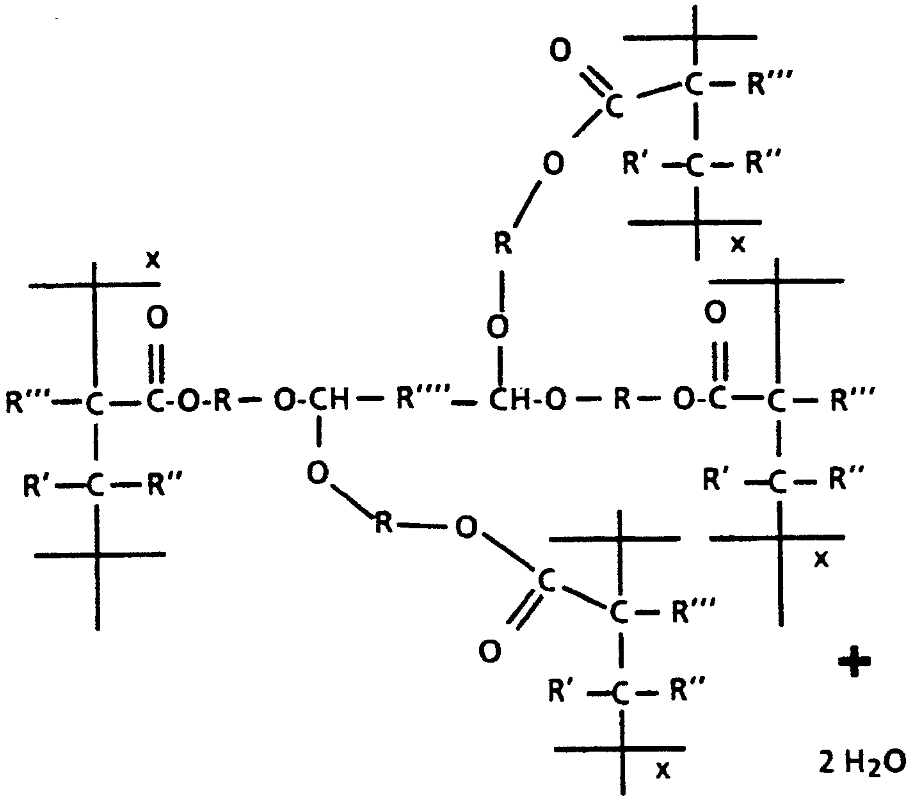
The initial reaction product from the chemical reaction of two hydroxyl groups (one from each chain) with both ends of a difunctional aldehyde is illustrated below:



to form hemiacetal linkages between two chains shown below:



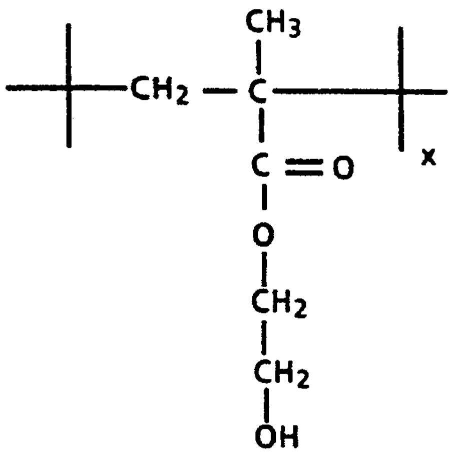
The two OH groups in the hemiacetal linkages can further combine with two more OH groups in the polymer repeat units (or can remain as is, which is already a crosslink) to give acetal crosslinks with the elimination of water as illustrated below:



The relative extent of hemiacetal and acetal crosslinking in dialdehyde crosslinked hydroxy ester polymer blocking layers is unknown. The higher the oven temperature during drying (solvent removal) of the blocking layer (up to a maximum of about 135° C.) and the longer the temperature is maintained at an elevated level (up to a practical maximum of about one hour) the more acetal linkages will form from the hemi-acetal linkages and other polymer repeat units and the higher will be the crosslink density. The monofunctional aldehydes (through acetal crosslinks only) can also be used to crosslink these hydroxy ester and hydroxy amide polymers but the crosslinking efficiency is less than that for the difunctional aldehyde because fewer crosslinks are formed per mole of monofunctional aldehyde versus difunctional aldehyde, all other factors being equal. Each time an acetal crosslink is formed, two hydroxyl groups in the hydroxy ester or hydroxy amide polymer are consumed. Thus, a high crosslink density can consume many hydroxyl groups which in turn will significantly reduce the H-bonding density and electron transport capability of these blocking layers. Thus, a minor amount of crosslinking with monofunctional aldehydes (through acetal crosslinks only) is acceptable, but too much could lead to V_R cycle-up (electron trapping). Crosslinking by hemiacetal crosslinks does not change the number of hydroxyl groups and is, therefore preferred. However, any other suitable technique may be utilized to crosslink hydroxy ester and hydroxy amide polymers through the hydroxyl groups. Generally, if catalysts are employed with the polyfunctional compounds, care should be taken to wash out the catalyst and avoid catalytic residues in the final blocking layer which might adversely affect electrical properties. Similarly, other permanent non-volatile residues which might interfere with the desired final electrical properties of the blocking layer should be avoided. This also ensures that there is no undesirable residue that could migrate out of the blocking layer or which could function as an electron trap in the blocking layer.

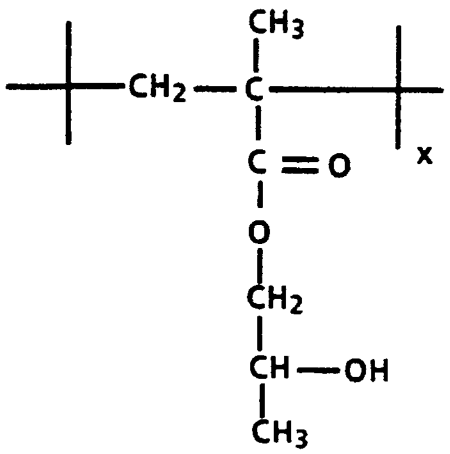
Satisfactory results may be achieved with vinyl hydroxy ester or vinyl hydroxy amide polymers having a weight average molecular weight of at least about 10,000, the upper limit being limited by the viscosity necessary for processing. Preferably, the weight average molecular weight is between about 20,000 and about 2,000,000. Optimum blocking layer performance is obtained when the weight average molecular weight is between about 100,000 and about 2,000,000. T_g or glass transition temperature has no known effect on the ability of a hole blocking layer of this invention to function effectively.

Optimum results are achieved with the vinyl hydroxy ester polymer poly(2-hydroxyethylmethacrylate) [P(HEMA)] which is represented by the following formula:



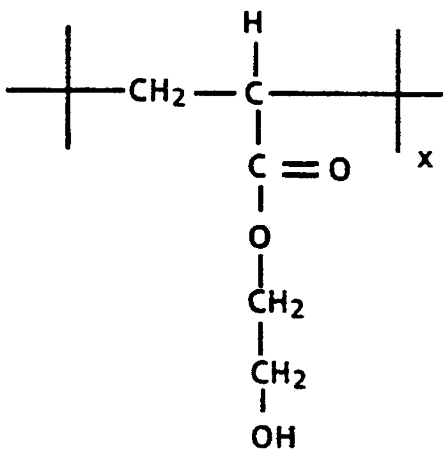
wherein x represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000.

Another preferred vinyl hydroxy ester polymer is poly(2-hydroxypropylmethacrylate) [P(HPMA)] which is represented by the following formula:



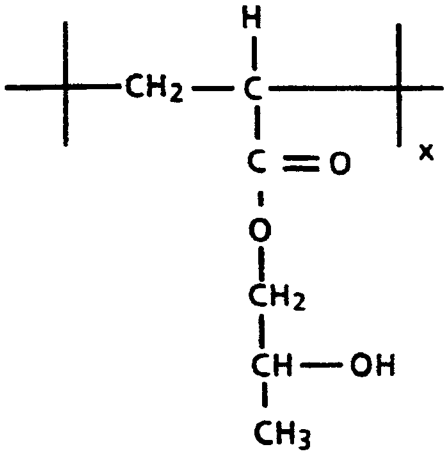
wherein x represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000.

Still another preferred **vinyl hydroxy ester** polymer is poly(2-hydroxyethylacrylate) [P(HEA)] which is represented by the following formula:



wherein x represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000.

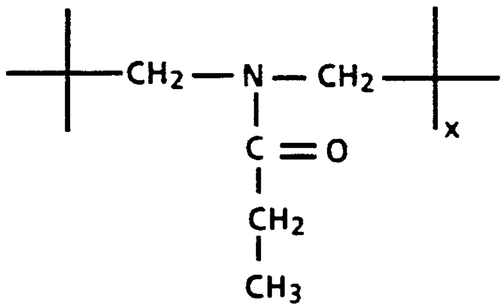
Still another preferred vinyl hydroxy ester polymer is poly(2-hydroxypropylacrylate) [P(HPA)] which is represented by the following formula:



wherein x represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000.

Compounds of this invention also include film forming copolymers of the above compounds with one or more copolymerizable vinyl or other suitable monomers. Typical copolymerizable vinyl monomers include acrylonitrile, methacrylonitrile, methylvinylether, and other alkyl and aryl vinyl ethers, styrene and substituted styrenes, ethylene, propylene, isobutylene, vinyl acetate, N,N-dimethylacrylamide, N-vinylpyrrolidone, 2, 3, and 4 vinylpyridine, various methacrylate and acrylate esters and vinyl chloride, and the like. Some monomers that undergo vinyl like polymerizations that are not vinyl monomers may also copolymerize with these hydroxy ester or hydroxy amide vinyl monomers. These include, for example, butadiene, isoprene, chloroprene, other conjugated diene monomers and the like. Generally, satisfactory results may be achieved with at least about 25 mole percent vinyl hydroxy ester or vinyl hydroxy amide repeat units in a copolymer. Specific examples of typical copolymers include those derived from 2-hydroxyethylmethacrylate and acrylonitrile; 2-hydroxyethylmethacrylate and N-vinylpyrrolidone, 2-hydroxypropylmethacrylate and N-vinylpyrrolidone, 2-hydroxyethylmethacrylate and 2-hydroxypropylmethacrylate, and the like.

The polymers of this invention may be blended with other compatible polymers. Compatible polymers are miscible with the vinyl hydroxy ester or vinyl hydroxy amide polymer of this invention. Typical miscible polymers include polyethyloxazoline (available from Dow Chemical Company) and any other sufficiently basic organic polymers capable of forming H-bonding complexes with hydroxyl groups sufficiently strong that phase separation is inhibited by the hydrogen bonding. It is believed that these basic organic polymers would include poly(ethylene and propylene) imines and other organic nitrogen containing basic polymers, but not poly(vinylpyridines). Polyethyloxyazoline may be represented by the following structural formula:



wherein x is a number from 300 to 20,000. Generally, satisfactory results may be achieved with at least about 25 percent by weight of vinyl hydroxy ester or vinyl hydroxy amide polymer in a blend with a polymer which does not contain any vinyl hydroxy ester polymer repeat units. A preferred blend concentration is is one containing at least about 75 percent by weight of the vinyl hydroxy ester or vinyl hydroxy amide polymer where the other polymer in the blend does not contain any vinyl hydroxy ester polymer repeat units. Optimum results are achieved with a concentration of 100 percent by weight of the vinyl hydroxy ester or vinyl hydroxy amide polymer. The minimum amount of vinyl hydroxy ester or vinyl hydroxy amide polymer to be blended can vary to some extent, depending upon what other repeat units are utilized.

The vinyl hydroxy ester or vinyl hydroxy amide polymers and copolymers of this invention are generally miscible with each other. Moreover, if a vinyl hydroxy ester or vinyl hydroxy amide copolymer contains at least 50 mole percent of hydroxy ester or hydroxy amide repeat units then this copolymer will be miscible with another vinyl copolymer containing at least 50 mole percent of the hydroxyester or hydroxyamide in the first copolymer; or if the second copolymer contains at least 50 mole percent of the non-hydroxy repeat unit of the first copolymer. In some cases, the common repeat unit, in the second copolymer, can be as low as 33 mole percent and miscibility is achieved. Miscibility is defined as a non-hazy coating (after drying) of equal amounts of the two copolymers cast from common solution of the two copolymers in one solvent. These are all random (not blocked) copolymers. The vinyl hydroxy ester (or amide) repeat unit content (expressed as weight percent) in a blend of two polymers, having a common vinyl hydroxy ester (or amide) repeat unit content of at least 33 mole percent in each polymer is preferrably between about 0.10 and 99.9 weight percent.

The specific composition selected for the ground plane will influence the thickness of the blocking layer selected. Generally, non-metallic or oxidizable charge injection ground plane materials require a thicker blocking layer. For example, a photoreceptor utilizing a charge injecting ground plane layer containing copper iodide without an overlying blocking layer merely charges to about 3 volts/micrometer. When a sufficiently thick blocking layer of this invention is applied over the ground plane layer containing copper iodide, the photoreceptor will charge to levels at least about 20 volts/micrometer. Charge levels of at least about 30 volts/micrometer are preferred with optimum results being achieved at levels of at least about 40 volts/micrometer. At levels below about 20 volts/micrometer, contrast potential decreases and lighter images cannot be developed with two-component dry xerographic developers.

The blocking layer mixture is applied to the conductive surface of the supporting substrate. The blocking layer mixture of this invention may be applied by any suitable conventional technique. Typical application techniques include spraying, dip coating, roll coating, wire wound rod coating, and the like. Coating compositions are usually applied with a solvent. Typical solvents include methanol, 1-methoxy-2-hydroxypropane, tertiary butyl alcohol, water and mixtures of these solvents with other alcohol solvents and tetrahydrofuran and the like. Choice of solvents depends upon the nature of the conductive layer upon which the barrier layer is applied and also on the properties of the polymers constituting the blocking layer. Appropriate solvents can, in general, be selected based on the known properties of the individual polymers, as is well known in the art. Mixtures of solvents may also be used, if desired. The proportion of solvent to be utilized varies with the type of coating technique to be employed, e.g., dip coating, spray coating, wire wound bar coating, roll coating, and the like so that the viscosity and volatility of the coating mixture is adjusted to the type of coating technique utilized. Generally, the amount of solvent ranges from between about 99.8 percent by weight to about 90 percent by weight, based on the total weight of the coating composition. Typical combinations of specific solvents and polymers include, for example, poly(2-hydroxyethylmethacrylate) and 1-methoxy-2-hydroxypropane (Dowanol PM, available from Dow Chemical Co.) or tertiary butyl alcohol. Basic alcohols such as dimethylaminoethanol and acidic alcohols such as 2,2,2-trifluoroethanol also dissolve poly(2-hydroxyethylmethacrylate) significantly at room temperature but solvent neutrality is usually desirable to avoid interference with the ground plane or other layers affecting photoreceptor electrical performance. High boiling dipolar aprotic solvents such as dimethylformamide, dimethylacetamide and N-methylpyrrolidone (DMF, DMAC and NMP respectively) also dissolve poly(2-hydroxyethylmethacrylate) extensively but are less desirable because total solvent removal from the coatings is more difficult to achieve due to the high boiling points of these solvents. Thus, there are a limited number of solvents suitable for coating high molecular weight hydroxy ester and hydroxy amide vinyl polymers. The limited solubility of high molecular weight vinyl hydroxy ester or vinyl hydroxy amide polymers in common organic solvents is desirable because the deposition of subsequent device layers, such as the generator layer from solutions using common solvents such as toluene and tetrahydrofuran and the transport layer using common solvents such as methylene chloride, does not cause extensive solvent induced migration of these hydroxy ester and hydroxy amide vinyl polymers from the blocking layer into the layers overlying the blocking layer.

The hydroxy ester and hydroxy amide vinyl polymers and copolymers of this invention have chemical structures containing hydroxyl groups which assist in retaining H_2O through hydrogen bonding. The combination of the presence of hydroxyl groups and a small amount of water are believed to assist in enabling hole blocking layers to function effectively during charging and photo discharging negatively charged photoreceptors. Moreover, the presence of the hydroxyl groups also provides the insolubility of the blocking layer towards the coating compositions deposited on top of the blocking layer such as the charge generating layer (applied with typical organic solvents such as toluene and tetrahydrofuran) and the charge transport layer (applied with typical organic solvents such as chlorinated alkane solvents, e.g. methylene chloride, 1,2-dichloroethane and 1,1,2-trichloroethane). If the blocking layer polymer is soluble in any of the organic solvents used in coating subsequent layers, the thickness uniformity and integrity thereof could be adversely affected because the organic solvents may wash the blocking layer material into the charge generating layer and/or charge transport layer. Thinner blocking layer or areas devoid of blocking layer material can result in very poor or even negligible device charge acceptance and high dark charge decay rate. The organic (non-hydroxyl containing) polymers described in US-A 4,410,614 would be too soluble in the above-mentioned organic solvents and, therefore, would not be suitable as blocking layers where the above-mentioned organic solvents are utilized with subsequently applied layers. Thus, for example, only a very limited number of organic solvents such as alcohols, glycol ethers and dipolar aprotic solvents can be utilized for the hydroxyl group containing polymeric blocking layer materials of this invention.

The molecular weight of the vinyl hydroxy ester or vinyl hydroxy amide polymer of this invention, as indicated by a dilute solution viscosity measurement, such as inherent viscosity, intrinsic viscosity, or reduced viscosity, is believed to be important in blocking layer applications because higher molecular weight polymers (all other things being equal) swell much more slowly than lower molecular weight polymers. Also, the use of higher molecular weight polymers in blocking layer applications allows the hydroxyl polymers to better encapsulate small molecules, such as water. Thus, longer chains of hydroxyl polymers can better encircle small water molecules and can better hydrogen bond these water molecules by providing more H-bonding sites per polymer chain when the polymer has a very high molecular weight. Also high molecular weight polymer chains can entangle (similar to spaghetti) with a larger number of contact sites than can low molecular weight polymer chains because the higher molecular weight polymer chains encompass or fill a larger volume of space. A contact site with the vinyl hydroxy ester or vinyl hydroxy amides of this invention means a hydrogen bonding site at another vinyl hydroxy ester (or amide) site in the same polymer chain or with a neighbor chain. Therefore, longer (or higher MW) polymer chains will have more contact or entanglement sites with more neighbor chains creating a denser and tighter H-bonding network to encapsulate small H-bonding molecules such as water. Therefore, even at low relative humidity (RH) conditions, very little water will migrate out of the high molecular weight hydroxyl polymer blocking layer thereby allowing the blocking layer to continue to function effectively even at low RH. Thus, devices containing the higher molecular weight blocking layers of this invention show only a minimal increase in V_R cycle-up at low RH. Moreover, during fabrication of the charge generating layer and/or charge transport layer, solvent contact with the surface of the blocking layer will cause less physical disruption of the top of the blocking layer when a high molecular weight polymer is utilized. This further preserves the thickness uniformity of the hole blocking layer and its ability to function effectively. Poly(2-hydroxylethylmethacylate) available from Scientific Polymer Products, has a molecular weight of about 1.0 to 1.4 x 10^6 based on dilute solution measurements wherein the reduced viscosity is 1.8 to 2.0 g/dl. Compared to the much lower viscosities, and thus molecular weights, of the polymers cited in US-A 4,410,614, a high molecular weight poly(2-hydroxylethylmethacylate) blooking layer of this invention is believed to have an intrinsic blocking layer advantage (because of a lower swelling rate) over the organic polymethacrylates described in US-A 4,410,614.

After the blocking layer coating is applied, the deposited coating is heated to drive out the solvent and form a solid continuous film. Generally, a drying temperature between about 110°C and about 135°C is preferred to minimize any residual solvent, to minimize any distortion to organic film substrates such as biaxially oriented polyethylene terephthalate. The temperature selected depends to some extent on the specific electrically conductive layer utilized and is limited by the temperature sensitivity of the substrate. The drying temperature may be maintained by any suitable technique such as ovens, forced air ovens, radiant heat lamps, and the like. The drying time depends upon the temperatures used. Thus, less time is required when higher temperatures are employed. Generally, increasing the drying time increases the amount of solvent removed. One may readily determine whether sufficient drying has occurred by chromatographic or gravimetric analysis. A typical treatment involves application of the coating with a half mil Bird coating bar followed by heating of the deposited coating at 130°C for about 10 to 30 minutes. Generally, satisfactory results may be achieved with a dried blocking layer coating having a thickness between about 0.05 micrometer and about 8 micrometers on some conductive layers. When the thickness of the layer exceeds about 8 micrometers, the electrophotographic imaging member may show poor discharge characteristics and residual voltage build-up after erase during cycling. A thickness of less than about 0.02 micrometer tends generally to result in pin holes as well as high dark decay and low charge acceptance due to non-uniformity of the thickness of different areas of the blocking layer. The preferred thickness range is between about 0.3 micrometer and about 1.5 micrometers with optimum blocking results being achieved with a thickness of between about 0.8 micrometer and about 1 micrometer on most conductive surfaces. The surface resistivity of the dry blocking layer of the present invention should be greater than about 10^{10} ohms/sq as measured at room temperature (25° C) and one atmosphere pressure under 40 percent relative humidity conditions. This minimum electrical resistivity prevents the blocking layer from becoming too conductive.

Some of the blocking layer materials of this invention can form a layer which also functions as an adhesive layer. However, if desired, an optional thin adhesive layer may be utilized between the relatively thick blocking layer and the charge generation layer. Any suitable adhesive material may be applied to the blocking layer. Typical adhesive materials include polyesters (e.g. 49000, available from E. I. duPont de Nemours & Co. and PE100 and PE200, available from Goodyear Tire & Rubber Co.) polyvinylbutyral, polyvinyl formal, polyvinylpyrolidone, polyamide, polyurethane, polyvinyl acetate, polyvinyl chloride, polyimide, polycarbonate, copolymers thereof, blends thereof and the like. Generally, satisfactory results may be achieved with adhesive layers having a thickness of between about 0.005 micrometer to about 0.2 micrometer. A preferred thickness is from about 0.02 micrometer to about 0.15 micrometer. Optimum results are achieved with a thickness of about 0.03 micrometer (300 angstroms) to about 0.12 micrometer from materials such as polyvinyl pyridine. When the thickness of the adhesive layer exceeds about 0.2 micrometer, residual voltage begins to cycle up excessively. Adhesive layers are especially useful for enhancing adhesion to charge generation layers containing materials, such as polyvinyl carbazole, which adhere poorly to vinyl hydroxy ester or vinyl hydroxy amide blocking layer polymers. Typical adhesive layer materials are those producing strong hydrogen bonds with vinyl hydroxy ester or vinyl hydroxy amide polymers such as poly(4-vinylpyridine), poly(2-vinylpyridine), and the like. Adhesive layers containing poly-(4-vinylpyridine) form a hydrogen bonded polymeric complex with vinyl hydroxy ester or vinyl hydroxy amide blocking layer polymers which are believed to be unique adhesive compositions having solubility properties which allow the adhesive layer to also function as a solvent barrier layer.

In US-A 4,082,551, an acidic polymer and a basic polymer are sequentially coated onto a substrate instead of a neutral polymer and a basic polymer as accomplished in one embodiment of this invention. This means that a polymeric salt complex forms in the device of US-A 4,082,551 whereas a hydrogen bonded polymeric complex is formed in one embodiment of this invention. The polymeric salt complex is a different composition of matter than the hydrogen bonded polymeric complex. More specifically, in US-A 4,082,551, a multilayer interlayer composition is disclosed comprising a lower layer (adjacent to the conductive layer) containing an acidic polymeric material (e.g. 0.4 micrometer layer of polyacrylic acid or methacrylic acid copolymer) and an upper layer (adjacent to the photogenerator layer) containing a basic polymeric material (e.g. 0.2 micrometer thick layer of a poly (2-vinylpyridine)-polymethylmethacrylate copolymer). At the polymeric interface of this multilayer-interlayer composition, an acid-base reaction product zone otherwise called a salt interlayer is generated. The total thickness of this complex multilayer interlayer composition can be between 0.2 micrometer to 1.0 micrometer and its function is to provide good adhesion between the conductive and photoconductive layers and to act as an electrical barrier blocking positive charge carrier injection (hole injection) from the conductive layer to the photoconductive layer. However, a major difference between the composite blocking/adhesive layer composition embodiment of the instant invention and that described in US-A 4,082,551 is that the instant invention embodiment utilizes, for example, a very thin (e.g. 0.06 micrometer) basic poly (4-vinylpyridine) adhesive enhancement component on top of a thicker (e.g. 0.2 to 1.5 micrometer) neutral vinyl hydroxy ester or vinyl hydroxy amide polymer hole blocking component. The presence of poly (4-vinylpyridine) component is not required to obtain high charge levels, (which is the same as preventing hole injection from the conductive layer to the photoconductive layer) but as a hydrogen bonded polymeric complex with the top of the vinyl hydroxy ester or vinyl hydroxy amide polymer hole blocking component. The poly (4-vinylpyridine)-vinyl hydroxy ester or vinyl hydroxy amide polymer interface also performs the functions of any interface material beneath the photogenerator layer. The vinyl hydroxy ester or vinyl hydroxy amide hole blocking component polymer alone performs these functions but the poly (4-vinylpyridine) enhances adhesion to generator layers. The poly (4-vinylpyridine)-vinyl hydroxy ester or vinyl hydroxy amide polymer adhesive interface also functions as a solvent barrier layer towards the solvents used to coat the layers above, and also readily accepts and transports photodischarged electrons when these photodischarged electrons arrive at the poly (4-vinylpyridine)-vinyl hydroxy ester or vinyl hydroxy amide polymer interface from the photogenerator layer. Although the projected thickness of the poly (4-vinylpyridine) layer is based on dried control coatings of known coating solution concentrations on glass plates, the actual thickness may vary depending on the depth of penetration of the poly (4-vinylpyridine) into the thick vinyl hydroxy ester or vinyl hydroxy amide polymer layer beneath. In a typical example, a draw bar coated (0.5 mil bar gap) poly (4-vinylpyridine) adhesive layer composition can consist of a 0.6 weight percent solution of 0.1 2g poly (4-vinylpyridine) (Reillene 4200, available from Reilly Tar and Chemical Co.) in 1 7.89g isobutanol and 1 .99g isopropanol. The drawbar coating process can be carried out on a previously dried vinyl hydroxy ester or vinyl hydroxy amide polymer blocking layer and the resulting poly (4-vinylpyridine) layer can similarly be dried for one hour under ambient conditions and then for on hour at 100°C in an air convection oven. The depth of penetration of the poly (4-vinylpyridine) polymer into the vinyl hydroxy ester or vinyl hydroxy amide polymer layer is largely a function of the solubility of the vinyl hydroxy ester or vinyl hydroxy amide polymer in the solvent (e.g. isobutanol-isopropanol mixture) used to apply the poly (4-vinylpyridine). Vinyl hydroxy ester or vinyl hydroxy amide polymers, such as poly (2-hydroxypropylmethacrylate), which has significant solubility in the above solvent mixture would be expected to imbibe the poly (4-vinylpyridine) to a larger penetration depth versus poly (2-hydroxyethylmethacrylate) which has almost no solubility in the alcoholic solvent mixture. Consequently, different thicknesses of the poly (4-vinylpyridine)-vinyl hydroxy ester or vinyl hydroxy amide polymer interface will result. It is expected that a gradient distribution of poly (4-vinylpyridine) in the poly (4-vinylpyridine)-vinyl hydroxy ester or vinyl hydroxy amide polymer interface layer occurs with the highest concentration of poly (4-vinylpyridine) chains near the top surface of the interlayer and the lowest concentration of poly (4-vinylpyridine) chains at the bottom of the interlayer where pure vinyl hydroxy ester or vinyl hydroxy amide polymer resides. After solvent evaporation from the poly (4-vinylpyridine) coating, hydrogen bonding between the poly (4-vinylpyridine) and the mixed and adjacent vinyl hydroxy ester or vinyl hydroxy amide polymer occurs thus anchoring the poly (4-vinylpyridine) chains into the interface layer composition. If the poly (4-vinylpyridine) is coated too thickly, poly (4-vinylpyridine) can migrate into the generator layer during subsequent coating steps and cause V_R cycle-up. Thus, too thick a coating of poly (4-vinylpyridine) can result in a surplus of poly (4-vinylpyridine) chains adjacent to each other and not adjacent to the vinyl hydroxy ester or vinyl hydroxy amide polymer chains where hydrogen bonding anchoring occurs. These unanchored poly (4-vinylpyridine) chains can migrate upward if solubilized by the solvents used to coat the subsequent layers above. Poly (4-vinylpyridine) hydrogen bonded to vinyl hydroxy ester or vinyl hydroxy amide polymer comprises an insoluble solvent barrier layer. Thus, an optimum coating concentration thickness of about 0.6 weight percent, as previously described, provides an extrapolated poly (4-vinylpyridine) coating thickness of 0.06 micrometer (not the poly (4-vinylpyridine)-vinyl hydroxy ester or vinyl hydroxy amide polymer interface thickness) which results in a totally hydrogen bonded poly (4-vinylpyridine) and an excellent adhesive solvent barrier interface layer. Such a poly (4-vinylpyridine)-vinyl hydroxy ester or poly (4-vinylpyridine)-vinyl hydroxy amide polymer interface layer of optimum poly (4-vinylpyridine) concentration in devices comprising a charge generation layer and a charge transport layer show little or no increase in V_R during charge-erase cycles.

In US-A 4,082,551, the acid-base reaction product formation described (Column 8, lines 32-53) involves taking equal weights of an acidic and basic polymer, individually dissolving them in methanol, and combining the two resulting solutions to form an insoluble reaction product. The insoluble reaction product is said to be indicative of the acid-base product zone formed at the interface of the acidic polymer layer and basic polymer layer present in the multilayer interlayer compositions. Furthermore in Column 7, lines 32-43, the patent states that "what is critical to the present invention is that the acid polymer layer contain polymer(s) which has sufficient acidity and that the basic polymer layer contain polymer(s) which has sufficient basicity such that an acid-base reaction product between these two layers can be formed at the interface thereof".

The above insoluble reaction product formation test was repeated using poly (2-hydroxyethylmethacrylate) (available from Polysciences) and poly (4-vinylpyridine) (Reillene 4200, available from Reilly Tar and Chemical Co.) in the same methanol solvent. However, in the product of the instant invention, the test is indicative of not an acid-base reaction product as described above in U.S. 4,082,551, but of a neutral hydrogen donor polymer poly (2-hydroxyethylmethacrylate) and a basic nitrogen polymer poly (4-vinylpyridine) hydrogen bonded polymeric complex, that is, the hydroxyl hydrogen is only partially transferred as a proton to the pyridine nitrogen to form the hydrogen bonded polymeric complex. Thus, the product of the instant invention is free of an acid-base reaction product as described above in U.S. 4,082,551.

In US-A 3,932,179 a multilayer electrophotographic element is disclosed comprising a conducting layer, a photoconductive layer, and a polymeric interlayer having a surface resistivity greater than about 10^{12} ohm/sq between the conducting layer and the photoconductive layer. The interlayer comprises a blend of at least two distinct polymeric phases comprising: (a) a film forming water or alkali-water soluble polymer and (b) an electrically insulating, film forming, hydrophobic polymer. For example, the conducting layer may contain cuprous iodide imbibed in a copolymeric binder of polymethylmethacrylate and polymethacrylic acid. A complex two phase hazy layer, composed of a complex terpolymer (65 wt. percent) of poly-(methylacrylate-vinylidene chloride-itaconic acid) and poly-(vinylmethylether maleic anhydride) (35 wt. percent) is employed as an organic solvent barrier, an adhesive aid, and a hole blocking layer. In column 4, line 47, type 3 polymers are described as polymers, including homopolymers and copolymers, comprising a backbone chain of repeating hydrocarbon units and acidic groups containing up to 10 carbon atoms as pendant side chains chemically bonded to the backbone chain. Useful acidic groups may be selected from the group consisting of sulfonic acids, carboxylic acids and carboxylic anhydrides. In column 4, line 54, it is indicated that pendant side chains composed of other groups, for example, such as hydroxy, alkoxy and ester groups having up to ten carbon atoms may also be present in the aforementioned type 3 polymers. In column 4, line 57, it is clear that typically, the type 3 polymers have at least 3 or more repeating units in the backbone chain. The list of these show no hydroxy groups in the polymer. In the type 3 polymers, the acidic group appears to be essential to the functioning of these materials as blocking layers. The presence of hydroxy groups in type 3 polymers is an incidental occurrence, not essential to the composition required to give an effective type 3 blocking layer. In addition, type 3 polymers have 3 or more repeat units in the backbone chain wherein an acid group must be contained in at least one of these repeat units. If an acid group is present (and it must be in all of the preferred type 3 copolymers (see bottom of column 4 and top of column 5 of US-A 3,932,179) the carboxylic acid group provides the water solubility or alkali solubility (pH 7 to 12) that the type 3 polymers must possess. The blocking layer polymers of the instant invention are generally not water soluble and nor do they need to be combined with a hydrophobic polymer. The preferred blocking layer of the instant invention generally contains a single component, that is, one polymer or copolymer, so it contains a very high concentration of hydroxyl groups (not incidental) and no acid groups for water solubility since water solubility is to be avoided. A satisfactory blocking layer of the instant invention generally comprises a lower concentration (as low as about 25 weight percent) of hydroxyl group containing repeat units, wherein the hydroxyl repeat unit content is diluted with non-hydroxyl containing repeat units in the same polymer (a copolymer) or in another polymer (a blend) or both. However, the lower hydroxyl repeat unit content is not incidental to obtaining improved photoreceptor cyclic electrical performance versus the same blocking layer composition wherein the hydroxyl repeat units have been omitted. However, higher (about 75-100 weight percent) hydroxyl repeat unit content will give preferred cyclic electrical performance. The blocking layer of the instant invention with the neutral hydroxyl blocking layer polymers achieves very dense H-bonding with numerous hydroxyl groups that the 2 component, blocking layers in US-A 3,932,179 cannot achieve because the amount of H-bonding in U.S. 3,932,179 blocking layer polymers are many fewer (COOH---HOOC) per chain than in a blocking layer polymer such as P(HEMA). The hydroxyl polymers [e.g. P(HEMA)] have an O-H group in every repeat unit whereas the terpolymer in US-A 3,932,179 has many fewer COOH groups because the itaconic acid (or any other acid containing repeat unit in these terpolymers) is only 1 of 3 repeat units in the backbone chain. After dilution with the second polymer component, the COOH group content may further decrease and, therefore, so will the acid---acid H-bonding density which was low initially.

Generally, as described above and hereinafter, the electrophotoconductive imaging member of this invention comprises a supporting substrate layer having an electrically conductive surface, a vinyl hydroxy ester or vinyl hydroxy amide polymer containing blocking layer and a photoconductive imaging layer. The photoconductive layer may comprise any suitable photoconductive material well known in the art. Thus, the photoconductive layer may comprise, for example, a single layer of a homogeneous photoconductive material or photoconductive particles dispersed in a binder, or multiple layers such as a charge generating overcoated with a charge transport layer. The photoconductive layer may contain homogeneous, heterogeneous, inorganic or organic compositions. One example of an electrophotographic imaging layer containing a heterogeneous composition is described in U.S. Patent 3,121,006 wherein finely divided particles of a photoconductive inorganic compound are dispersed in an electrically insulating organic resin binder. The entire disclosure of this patent is incorporated herein by reference. Other well known electrophotographic imaging layers include amorphous selenium, halogen doped amorphous selenium, amorphous selenium alloys including selenium arsenic, selenium tellurium, selenium arsenic antimony, and halogen doped selenium alloys, cadmium sulfide and the like. Generally, these inorganic photoconductive materials are deposited as a relatively homogeneous layer.

This invention is particularly desirable for electrophotographic imaging layers which comprise two electrically operative layers, a charge generating layer and a charge transport layer.

Any suitable charge generating or photogenerating material may be employed as one of the two electrically operative layers in the multilayer photoconductor embodiment of this invention. Typical charge generating materials include metal free phthalocyanine described in U.S. Patent 3,357,989, metal phthalocyanines such as copper phthalocyanine, vanadyl phthalocyanine, selenium containing materials such as trigonal selenium, bisazo compounds, quinacridones, substituted 2,4-diamino-triazines disclosed in U.S. Patent 3,442,781, and polynuclear aromatic quinones available from Allied Chemical Corporation under the tradename Indofast Double Scarlet, Indofast Violet Lake B, Indofast Brilliant Scarlet and Indofast Orange. Other examples of charge generator layers are disclosed in U.S. Patent 4,265,990, U.S. Patent 4,233,384, U.S. Patent 4,471,041, U.S. Patent 4,489,143, U.S. Patent 4,507,480, U.S. Patent 4,306,008, U.S. Patent 4,299,897, U.S. Patent 4,232,102, U.S. Patent 4,233,383, U.S. Patent 4,415,639 and U.S. Patent 4,439,507. The disclosures of these patents are incorporated herein by reference in their entirety.

Any suitable inactive resin binder material may be employed in the charge generator layer. Typical organic resinous binders include polycarbonates, acrylate polymers, vinyl polymers, cellulose polymers, polyesters, polysiloxanes, polyamides, polyurethanes, epoxies, and the like. Many organic resinous binders are disclosed, for example, in U.S. Patent 3,121,006 and U.S. Patent 4,439,507, the entire disclosures of which are incorporated herein by reference. Organic resinous polymers may be block, random or alternating copolymers. The photogenerating composition or pigment is present in the resinous binder composition in various amounts. When using an electrically inactive or insulating resin, it is essential that there be particle-to-particle contact between the photoconductive particles. This necessitates that the photoconductive material be present in an amount of at least about 15 percent by volume of the binder layer with no limit on the maximum amount of photoconductor in the binder layer. If the matrix or binder comprises an active material, e.g. poly-N-vinylcarbazole, the photoconductive material need only to comprise about 1 percent or less by volume of the binder layer with no limitation on the maximum amount of photoconductor in the binder layer. Generally for charge generator layers containing an electrically active matrix or binder such as polyvinyl carbazole or phenoxy resin [poly(hydroxyether)], from about 5 percent by volume to about 60 percent by volume of the photogenerating pigment is dispersed in about 40 percent by volume to about 95 percent by volume of binder, and preferably from about 7 percent to about 30 percent by volume of the photogenerating pigment is dispersed in from about 70 percent by volume to about 93 percent by volume of the binder The specific proportions selected also depends to some extent on the thickness of the generator layer.

The thickness of the photogenerating binder layer is not particularly critical. Layer thicknesses from about 0.05 micrometer to about 40.0 micrometers have been found to be satisfactory. The photogenerating binder layer containing photoconductive compositions and/or pigments, and the resinous binder material preferably ranges in thickness of from about 0. 1 micrometer to about 5.0 micrometers, and has an optimum thickness of from about 0.3 micrometer to about 3 micrometers for best light absorption and improved dark decay stability and mechanical properties.

Other typical photoconductive layers include amorphous or alloys of selenium such as selenium-arsenic, selenium-tellurium-arsenic, selenium-tellurium, and the like.

The active charge transport layer may comprise any suitable transparent organic polymer or non-polymeric material capable of supporting the injection of photo-generated holes and electrons from the charge generation layer and allowing the transport of these holes or electrons through the organic layer to selectively discharge the surface charge. The active charge transport layer not only serves to transport holes or electrons, but also protects the photoconductive layer from abrasion or chemical attack and therefore extends the operating life of the photoreceptor imaging member. The charge transport layer should exhibit negligible, if any, discharge when exposed to a wavelength of light useful in xerography, e.g. 4000 Angstroms to 8000 Angstroms. Therefore, the charge transport layer is substantially transparent to radiation in a region in which the photoconductor is to be used. Thus, the active charge transport layer is a substantially non-photoconductive material which supports the injection of photogenerated holes or electrons from the generation layer. The active transport layer is normally transparent when exposure is effected through the active layer to ensure that most of the incident radiation is utilized by the underlying charge carrier generator layer for efficient photogeneration. When used with a transparent substrate, imagewise exposure may be accomplished through the substrate with all light passing through the substrate. In this case, the active transport material need not be absorbing in the wavelength region of use. The charge transport layer in conjunction with the generation layer in the instant invention is a material which is an insulator to the extent that an electrostatic charge placed on the transport layer is not conductive in the absence of illumination, i.e. does not discharge at a rate sufficient to prevent the formation and retention of an electrostatic latent image thereon.

The active charge transport layer may comprise an activating compound useful as an additive dispersed in electrically inactive polymeric materials making these materials electrically active. These compounds may be added to polymeric materials which are incapable of supporting the injection of photogenerated holes from the generation material and incapable of allowing the transport of these holes therethrough. This will convert the electrically inactive polymeric material to a material capable of supporting the injection of photogenerated holes from the generation material and capable of allowing the transport of these holes through the active layer in order to discharge the surface charge on the active layer.

An especially preferred transport layer employed in one of the two electrically operative layers in the multilayer photoconductor embodiment of this invention comprises from about 25 to about 75 percent by weight of at least one charge transporting aromatic amine compound, and about 75 to about 25 percent by weight of a polymeric film forming resin in which the aromatic amine is soluble.

Examples of charge transporting aromatic amines represented by the structural formulae above for charge transport layers capable of supporting the injection of photogenerated holes of a charge generating layer and transporting the holes through the charge transport layer include triphenylmethane, bis(4-diethylamine-2-methylphenyl) phenylmethane; 4'-4"-bis(diethylamino)-2',2"-dimethyltriphenyl-methane, N , N'-bis(alkylphenyl)-[1,1'-biphenyl]-4,4'-diamine wherein the alkyl is, for example, methyl, ethyl, propyl, n-butyl, etc., N,N'-diphenyl-N,N'-bis(chlorophenyl)-[1,1'-biphenyl]-4,4'-diamine, N,N'-diphenyl-N,N'-bis(3"-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine, and the like dispersed in an inactive resin binder.

Any suitable inactive resin binder soluble in methylene chloride or other suitable solvent may be employed in the process of this invention. Typical inactive resin binders soluble in methylene chloride include polycarbonate resin, polyvinylcarbazole, polyester, polyarylate, polystyrene, polyacrylate, polyether, polysulfone, and the like. Molecular weights can vary from about 20,000 to about 1,500,000.

The preferred electrically inactive resin materials are polycarbonate resins have a molecular weight from about 20,000 to about 100,000, more preferably from about 50,000 to about 100,000. The materials most preferred as the electrically inactive resin material is poly(4,4'-dipropylidene-diphenylene carbonate) with a molecular weight of from about 35,000 to about 40,000, available as Lexan 145 from General Electric Company; poly(4,4'-isopropylidene-diphenylene carbonate) with a molecular weight of from about 40,000 to about 45,000, available as Lexan 141 from the General Electric Company; a polycarbonate resin having a molecular weight of from about 50,000 to about 100,000, available as Makrolon from Farbenfabricken Bayer A.G., a polycarbonate resin having a molecular weight of from about 20,000 to about 50,000 available as Merlon from Mobay Chemical Company and poly(4,4'-diphenyl-1,1-cyclohexane carbonate). Methylene chloride solvent is a particularly desirable component of the charge transport layer coating mixture for adequate dissolving of all the components and for its low boiling point. However, the type of solvent selected depends on the specific resin binder utilized.

In all of the above charge transport layers, the activating compound which renders the electrically inactive polymeric material electrically active should be present in amounts of from about 15 to about 75 percent by weight.

If desired, the charge transport layer may comprise any suitable electrically active charge transport polymer instead of a charge transport momomer dissolved or dispersed in an electrically inactive binder. Electrically active charge transport polymer employed as charge transport layers are described, for example in US-A 4,806,443, US-A 4,806,444, and US-A 4,818,650, the entire disclosures thereof being incorporated herein by reference.

Any suitable and conventional technique may be utilized to mix and thereafter apply the charge transport layer coating mixture to the charge generating layer. Typical application techniques include spraying, dip coating, roll coating, wire wound rod coating, and the like. Drying of the deposited coating may be effected by any suitable conventional technique such as oven drying, infra red radiation drying, air drying and the like. Generally, the thickness of the transport layer is between about 5 micrometers to about 100 micrometers, but thicknesses outside this range can also be used.

The charge transport layer should be an insulator to the extent that the electrostatic charge placed on the charge transport layer is not conducted in the absence of illumination at a rate sufficient to prevent formation and retention of an electrostatic latent image thereon. In general, the ratio of the thickness of the charge transport layer to the charge generator layer is preferably maintained from about 2:1 to 200:1 and in some instances as great as 400:1.

Optionally, an overcoat layer may also be utilized to improve resistance to abrasion. In some cases a back coating may be applied to the side opposite the photoreceptor to provide flatness and/or abrasion resistance. These overcoating and backcoating layers may comprise organic polymers or inorganic polymers that are electrically insulating or slightly semi-conductive.

Thus, this invention extends the life of electrostatographic imaging members. The high molecular weight vinyl hydroxy ester or vinyl hydroxy amide polymers of this invention contain a hydroxyl group and carbonyl containing (ester, amide) functionality in each repeat unit for blocking hole injection in the dark and transporting photodischarged electrons. The blocking layers of this invention form a solvent barrier layer to most of the commonly used coating solvents used to coat the layers overlying the blocking layer, e.g. is substantially insoluble in solvents such as toluene, tetrahydrofuran and methylene chloride. The expression "substantially insoluble" as employed herein is defined as not sufficiently soluble to erode away a blocking layer in the time period that these solvents are in contact with the blocking layer so that high charge acceptance (V_0) and low (V_R) are retained in at least 200 consecutive imaging cycles. High V_0 is defined as at least 600 volts and low V_R is defined as less than about 100 volts. It is electrically hole blocking during and after corotron charging prior to photodischarge. It is also more dark stable. This prevents ground plane hole injection and enables high V_O charging initially and with repetitive cycling. The blocking layers of this invention electrically accept photodischarged electrons from the generator layer and transport most or all of the accepted electrons to the ground plane to complete the discharge process. Thus, the electrostatographic imaging member of this invention allows photodischarge with low residual voltage during cycling under most ambient relative humidities. This enables total discharge within the xerographic time scale, and thus low V_R initially and with repetitive cycling. The high molecular weight vinyl hydroxy ester or vinyl hydroxy amide polymers of this invention also afford sufficiently thick blocking layers in one or two spray passes from low viscosity, more concentrated solutions compared to other materials such as viscous poly-(vinylalcohol) aqueous solutions which require numerous spray coating passes to build up blocking layer dry thickness to the desired level. In addition, the co-presence of the carbonyl functionality in each repeat unit enhances hydroxy polymer solubility (versus PVOH) to generally include lower alcohols and glycol ethers as optional spray solvents which make higher quality coatings more likely. Further, after solvent evaporation the hydroxy polymers, because of their dipole interactions (ester, amide) with the conductive layer polymers, enhance solid state adhesion at this interface compared to materials such as poly-(vinylalcohol). A particularly surprising aspect of the high molecular weight blocking layers of this invention is the lack of a strong dependence upon a large amount of H-bonded water to assist photodischarged electron injection and transport. Devices containing the high molecular weight blocking layers of this invention can function independent of relative humidity without the need to provide an enclosed humidifier in the xerographic engine.

A number of examples are set forth herein below and are illustrative of different compositions and conditions that can be utilized in practicing the invention. All proportions are by weight unless otherwise indicated. It will be apparent, however, that the invention can be practiced with many types of compositions and can have many different uses in accordance with the disclosure above and as pointed out hereinafter.

EXAMPLE 1

The hole blocking capability of the various vinyl hydroxy ester or vinyl hydroxy amide containing polymeric materials used as blocking layers were evaluated to establish the hole injecting capability of various non-metallic conductive layers. This was accomplished in this Control Example by measuring the first cycle surface voltage in the dark immediately after corotron charging (~0.2 seconds) photoreceptors not containing a hole blocking layer. This value was thereafter compared in the following Examples to the first cycle surface voltage obtained on an otherwise identical photoreceptor, but with the polymeric hole blocking layer included. The larger the difference [$V_{o(1)}$ with blocking layer $V_{o(1)}$ without blocking layer] in measured voltages under a constant set of electrical testing conditions for two photoreceptors having approximately the same layer thicknesses and same conductive layer, the larger is the intrinsic ability of the hole blocking layer material to block hole injection. The photoreceptors were fabricated without hole blocking layers in this Example and with hole blocking layers in all the remaining Examples. The conductive layers used in this evaluation consisted of a conductive material, usually (but not always) dispersed in an insulative polymeric binder, at a given loading level (>10 weight percent) sufficient to function as a conductive ground plane in discharging the photoreceptor over many consecutive charge-erase (discharge) cycles.

Carbon Impregnated Tedlar® (CIT) Conductive Layer

A 3 mil thick conductive composite film (CIT) of conductive carbon impregnated in polyvinylfluoride (PVF) (commercially available from E.I. duPont De Nemours & Co.) was coated with the overlying photoreceptor layers. The CIT combines the functions of the conductive layer with the polymeric substrate into one layer. The expression CIT refers to carbon impregnated Tedlar®. Tedlar® is polyvinylfluoride without carbon black dispersed in it (also available from,E.I. duPont De Nemours & Co.). The loading level of the conductive carbon black in carbon impregnated Tedlar® was between 10-25 weight percent, and the film physically and electrically resembles polyvinylfluoride loaded with 15 weight percent conductive carbon black Black Pearls 2000(available from Carbot Corp.). CIT has sufficiently conductive resistivity ($\leq 10^5$ ohms/square), when measured with a four point probe, to be used successfully in numerous consecutive xerographic charge-discharge cycles.

Polyvinylfluoride coatings, with or without impregnated conductive carbon black, are chemically and physically resistant to common organic solvents (below 100° C) such as methylene chloride, tetrahydrofuran (THF), and toluene which are frequently used coating solvents for the other layers in these devices. In addition, the same PVF coatings are similarly solvent resistive to the more polar solvents such as lower alcohols (methanol, ethanol, isopropanol, n-butanol, sec. butanol and isobutanol) and ketones (acetone, methylethyl ketone and methyl isobutyl ketone) and water.

Crosslinked Carboset®/Carbon Black Conductive Layer

Conductive layer carbon black formulations were developed for both drawbar and spray coating fabrication. The drawbar coated formulation consisted of 6.87 grams polyacrylic resin (Carboset® 514A, available from B.F. Goodrich Co. as a 70% solution in isopropanol) diluted with 20.4 grams isopropanol and 7.5 grams methylisobutyl ketone (MIBK). To this solution was added 0.94 grams of a conductive carbon black (Black Pearls® 2000 from Cabot Corp.) which was suspended with a Paint Shaker (Red Devil, Inc. Model 5100X) for 90 minutes. Finally 0.51 gram of XAMA-2 (a Carboset crosslinking agent available from Virginia Chemicals) was added and the dispersion was shaken for 15 minutes on the paint shaker. The resulting carbon black dispersion with crosslinking agent was drawbar coated (2 mil gap) using a Model P290 Gardner Labs, Inc. 8 1/2" x 11" drawbar coater now available from Paciific Scientific. This carbon black conductive layer dispersion was coated onto insulative polymeric substrates, such as duPont's Tedlar® or Mylar film or Melinex Polyester (ICI), and was then dried for one hour ambiently and one hour at 100-120° C. in an air convection oven.

The dry thickness of the conductive layer was about 10 ± 5 micrometers wherein the useful conductivity range was not a function of thickness. The resulting dried conductive layer was a crosslinked network wherein the conductive carbon black particles are trapped in the polymeric network.

Carboset-carbon black conductive layers were also spray coated onto insulative polymeric substrates (e.g. Tedlar®, Mylar, Melinex®). The dispersion formulation used in spray coating was 80 grams Carboset 514A, 9.9 grams Black Pearls® 2000 conductive carbon black, 400 grams isopropanol and 1000 grams methylisobutyl ketone. All solvents used in this work were reagent grade. The above dispersion was roll milled with glass beads, for 64 hours. After decanting away the dispersion from beads, 8.4 grams XAMA-2 (the crosslinking agent) was added and magnetically stirred into the dispersion for 0.25 hour. The dispersion was sprayed using commercially available spray guns and equipment manufactured by Binks Manufacturing Company. A Binks Model 21 automatic spray gun was used in a Binks spray booth Model BF-4 with a type 42753 reciprocator. The Model 21 gun was equipped with a 63B fluid nozzle and a 63 PE air atomization nozzle. The fluid pressure was 4 psi and the spray atomization pressure was 50 psi. The needle setting was at 1.5 turns and the spray fan angle at 0.75 turns. These settings were counted from the closed position. The spray gun was operated in an automatic mode and was traversed on a reciprocator while spraying from top to the bottom of the vertically positioned mandrel. The insulative polymeric substrates sprayed were tape mounted and rotated on a cylindrical aluminum mandrel positioned on a shaft connected to a turntable. The conductive dispersion was spray cycled three times with 1.5 minutes elapsing between passes. Finally, the coating was removed from the mandrel and was dried at 120° C. for 0.5 hour in an air convection oven. Thus, the crosslinked conductive layer (drawbar or spray coated) functions as a solvent barrier preventing erosion thereof by subsequently used coating compositions and their solvents. Because of the maintained layer integrity, proper xerographic charging and discharging results over thousands of cycles.

The crosslinking chemistry between XAMA-2 and Carboset® 514A is explicitly illustrated in a technical brochure published by the B.F. Goodrich Co. entitled Carboset Resins for Permanent Coatings.

Black Conductive Olefinic Flash Primer LE16610 Conductive Layer

A conductive carbon black and a polymeric resin in a 60/40 by volume solvent mixture of toluene and xylene (Black Conductive Olefinic Flash Primer LE16610, available from the Red Spot Paint and Varnish Co., Inc.) was spray coated as received (without dilution) to give a 10-16 micrometer thick conductive layer that was sufficiently conductive to function as a ground plane for numerous consecutive xerographic charge-discharge cycles.

The LE16610 black conductive olefinic flash primer (600 grams) was also redispersed (≧0.5 hour.) using the previously described paint shaker (no steel shot or glass beads used). To spray a 12 micrometer thick (after drying) coating, four passes were applied according to the following set of spray parameters.

Atomization Pressure:	55psi
Fluid Pressure:	6psi
Fan Angle:	0.75 turns from closed position
Fluid Opening:	1.25 turns from closed position

The previously described spray guns and associated equipment manufactured by the Binks Manufacturing Company were also used to spray this conductive layer composition on the same insulative polymeric substrates, mounted as previously described. The coated substrates were then ambiently air dried for 1-16 hours and at 90° C. in an air convection oven for at least 0.25 hour.

Polypyrrole ICP-117 Conductive Layer

In a typical formulation for drawbar coating a conductive layer, 20 grams of Polaroid ICP-1 17 polypyrrole-polymer complex at 10 weight percent in ethylacetate was diluted with 10 grams of the same solvent. This dispersion was drawbar coated (0.5 mil gap) with the previously described Gardner coating apparatus onto an insulative polymeric substrate, such as Mylar or Tedlar® from duPont. The coated conductive layer on the insulative polymeric substrate was transferred to an air convection oven maintained at 100-120° C. for .5 to 1.0 hour to evaporate the coating solvent. Polaroid ICP-117 polypyrrole-polymer complex is negatively charged and the polypyrrole fragments are positively charged. However numerous copolymer compositions were employed which were capable of being charged negatively and these are described in two publications: (1) S.J. Jasne and C.K. Chiklis, Synthetic Metals, 15 175-182 (1986) and (2) European Patent Application, No. 85103447.0 filed 3/23/85.

Copper Iodide Conductive Layer

Conductive layers were drawbar and spray fabricated from commercially available copper iodide. The coatings prepared by drawbar fabrication will first be described.

Ultra pure cuprous iodide (2.30 grams) available from most chemical suppliers such as Aldrich Chemical Co. and Alfa-Ventron Research Chemicals and Materials, was mixed with pure butyronitrile solvent (100 ml) and the mixture was magnetically agitated for 4-16 hours at room temperature until a saturated solution formed. The trace amount of excess undissolved cuprous iodide was removed in a pressured (40 psi) filtration through a Nuclepore Filinert polycarbonate membrane (47 mm diameter) having a porosity of 0.2 microns. The clear filtrate was drawbar coated using a 6 mil bar gap and the coating was dried for one hour ambiently and then for at least 10 minutes in an air convection oven at 100° C. The dried coating thickness ranged from 200-1000 Angstroms as measured with an Auto EL elipsometer (Rudolph Research) at a wavelength of 6328 Angstrom.

The spray fabricated conductive copper iodide coatings are next described. To one liter of reagent grade butyronitrile solvent was added 23 grams of ultra pure cuprous iodide and the mixture was magnetically agitated at room temperature for two hours. The resulting solution [2.3 weight solute/volume solvent percent (w/v %)] was pressure filtered through a 0.2 micrometer Nuclepore filter at about 40 psi, and the filtrate was spray coated in 1 or 2 passes on either Mylar or Tedlar substrates. The transparent cuprous iodide coating ranged in thickness from 50 to 500 Angstroms.

The following set of spray parameters were used to spray the above solution in 2 passes:

Atomization Pressure:	55 psi
Fluid Pressure:	5 psi
Fan Angle:	0.75 turns from closed position
Fluid Opening:	0.75 turns from closed position.

The previously described spray guns and associated equipment manufactured by the Binks Manufacturing Company were used to spray this conductive layer composition, mounted as previously described. The sprayed conductive layers were allowed to ambiently dry for at least one hour and were then air convection oven dried for at least 0.5 hour.

Optionally a mixed nitrile saturated solution, comprising 515 ml butyronitrile, 345 ml acetonitrile (60:40 by volume) and 23.2 g cuprous iodide (2.7 w/v %), was filtered as described above and the filtrate was spray coated in 1 or 2 passes (1.5 minutes between passes) to give conductive layer coatings as described above for the single solvent spray solution. Similar drying conditions were employed but the spray parameters were slightly different:

Atomization Pressure: 5Spsi
Fluid Pressure: 4psi
Fan Angle: 0.5 turns from closed position

Fluid Opening: 0.5 turns from closed position.

These spray fabricated CuI coatings were found to be equally useful to drawbar coated CuI conductive layers.

The above conductive layers were fabricated (drawbar or sprayed) or used in the as received coated form (such as carbon impregnated Tedlar) as ground planes on which the other photoreceptor layers were fabricated. In this Example the vinyl hydroxy ester and vinyl hydroxy amide polymer blocking layers were deliberately omitted to establish the hole injection severity of representative conductive layer coatings. The devices fabricated in this example did not contain an adhesive layer between the conductive layer and the photogenerator layers except when the conductive layer was binderless cuprous iodide. In this case delamination occurred between the cuprous iodide layer and the photogenerator layer with routine handling of the completed device. To avoid delamination and thereby obtain charge-erase electrical evaluation, a very thin (<0.1 micrometer) poly(4-vinylpyridine) [P(4VPy)] adhesive layer was drawbar coated between the conductive layer and photogenerator layer. A typical poly(4 vinylpyridine) adhesive layer formulation consisted of a 0.6 weight percent solution of 0.12g Reillene® 4200 (Reilly Tar & Chemical Co.) in 17.89g isobutanol and 1 .99g isopropanol. After applying this solution as a coating with a 0.5 mil drawbar gap, using the previously described Gardner coating apparatus, the coating was dried ambiently for one hour and then for one hour at 100° C. in an air convection oven (standard conditions). When the poly(4 vinylpyridine) adhesive layer was drawbar fabricated in devices of subsequent examples, the above formulation, coating procedure and drying conditions were used unless otherwise indicated.

A charge generator layer mixture was prepared by forming a dispersion of about 8.57g trigonal selenium particles doped with about 1-2 percent by weight sodium hydroxide, 16.72g polyvinylcarbazole, 4.93g N,N'-bis-(3"-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine, 100. 55g tetrahydrofuran and 100.55g toluene. This dispersion was then diluted with an equal weight of toluene. The diluted dispersion was next agitated on a wrist shaker for about 5 minutes immediately prior to coating the conductive layer with a 1 ml drawbar gap. The charge generator coating was next dried for one hour at room temperature and for one hour at 100° C in an air convection oven. The dry thickness of the photogenerator layer thus obtained was about 1.0 ± 0.3 micrometer in this and subsequent Examples.

A charge transport layer coating mixture was prepared by mixing about 2.8g N,N'-bis(3"methylphenyl)-[1,1'-biphenyl]-4,4"-diamine, 4.2g polycarbonate resin (Makrolon® 5705, available from Farbenfabricken Bayer A.G.) and 40g methylene chloride. This mixture was coated with a 5 mil drawbar gap onto the photogenerator layer. The transport layer coating was dried at room temperature for one hour, and then through an incremental heating cycle from 50 to 100° C. in 0.50 to 0.75 hour and finally at 110° C. for at least 10 minutes. The dry thickness of the charge transport layers in this and subsequent Examples was about 25-30 micrometers as determined with a type DS No. 11033 Permoscope. The completed devices were electrically charge-erase cycled using either an ambient scanner or an environmental scanner which are described below.

The ambient cyclic scanner used to obtain the charge-erase cycling results, was equipped with a single wire corotron (5 cm wide) set to deposit 9 x 10^{-8} coulombs/cm^2 of charge on the surface of these experimental devices. The devices were grounded to an aluminum drum having a 76.5 cm circumference and the drum was rotated at a speed of 12 rpm giving a surface speed of 6 inches per second. The devices were discharged (erased) with a tungsten white light source emitted through a plexiglass light pipe and the intensity of the erase lamp was varied from 2 to 10X the amount of light required to discharge the device down to twice the asymptotic residual voltage. The entire xerographic simulation (charge and erase) was carried out in a light tight enclosure. Some environmental changes, such as low RH via purging with dry air and high RH via purging with moist air were made during some of the tests to obtain cyclic results under non-ambient conditions.

The environmental cyclic scanner used to obtain charge-erase cycling results under various environmental conditions, was equipped with a single wire corotron (5 cm wide) set to deposit 9 x 10^{-8} coulombs/cm^2 (or 14 x -10^{-8} coulombs/cm^2 in some cases) of charge on the surface of these experimental devices. The devices were grounded to an aluminum drum having a 63.1 cm circumference and the drum was rotated at a speed of 20 rpm to produce a surface speed of 8.3 inches per second. The devices were discharged (erased) with a short arc white light source emitted through a fiber optic light pipe. The entire xerographic simulation (charge and erase) was carried out in an environmentally controlled light tight chamber. The devices, without blocking layers in this Example, were charge-erase tested for 200 cycles at ambient RH. Ambient RH for all devices charge-erase cycled in this application was between 12 and 60%. Low RH charge-erase testing conditions when used were ≤5% and the test was run after first equilbrating the devices at low RH overnight.

TABLE A

Device #	Conductive Layer (Fabrication Method)	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
Ia	duPont CIT (prefabricated)	420	330	32	36
Ib	B.F. Goodrich Carboset® 514A (drawbar)	460	---	10	---
Ic	Red Spot® LE16610 (sprayed)	600	440	36	65
Id	Polaroid ICP-117 (drawbar)	200	180	22	25
Ie	CuI (drawbar)	90	90	4	4

The ambient cyclic scanner was employed to produce the data in TABLE A. This data in TABLE A indicates inferior charging levels [$V_{O(1)}$]. After charging these photoreceptors in the dark, hole injection from the conductive layer was unimpeded (no hole blocking layer) and so the negative surface charge was extensively neutralized prior to the first voltage measurement (~0.2 sec. after charging). The numerous examples which follow will show major improvement in the initially measured voltage [higher $V_{O(1)}$] and in retention of V_O after 200 cycles or more because of the use of suitable hole blocking layer materials interposed between the conductive layer and the photogenerator layer.

EXAMPLE II

This Example demonstrates the selection of a preferred poly(4 vinylpyridine) [P(4VPy)] thickness (coating concentration) as an adhesive layer between poly(2-hydroxyethylmethacrylate) [P(HEMA)] blocking layers and generator layers containing trigonal selenium particles dispersed in polyvinyl carbazole (PVK). When the P(4VPy) adhesive layer is too thick or is bulk mixed into the P(HEMA) to give phase separated (immiscible) blocking layer compositions, V_R cycle-up is immediately apparent (see following TABLE B). In contrast devices IIc & IId (described in detail below), which have no P(4VPy) adhesive layer, have no significant V_R cycle-up. All the P(4VPy) containing devices (IIa & IIb) in the Table B of this Example show considerable V_R cycle-up suggesting the P(4VPy) generates V_R cycle-up. The layered P(4VPy) containing devices (IIa and IIb) exhibit a smaller V_R cycle-up than the mixed P(4VPy)-P(HEMA) devices (IIe - IIg) implying a second mechanism for V_R cycle-up may be operative in the mixed blocking layer devices.

The V_R cycle-up in both the layered and mixed devices arises to some extent from P(4VPy) migration into the generator and/or transport layer during coating of these layers. The migrated P(4VPy) polymer in the generator and/or transport layer traps holes during device discharge thus causing V_R cycle-up. The P-(4VPy) migration is more prevalent when larger amounts (thicker layers) of P(4VPy) are present in the adhesive composition. Since P(4VPy) is methylene chloride soluble, considerable migration of P(4VPy) occurs during coating of the transport layer. Some of the P(4VPy) directly in contact with P(HEMA) will not migrate because the strong H-bonding interaction between the P(4VPy) and the P(HEMA) will anchor the former. However, when an excess amount of P(4VPy) reside in the P(HEMA), solvent assisted P(4VPy) migration still occurs because there is an insufficient number of H-bonds per polymer chain, on the average, to anchor all the P(4VPy) polymer in the P(HEMA).

The second V_R cycle-up mechanism, which occurs primarily in devices having a mixed P(4VPy)-P-(HEMA) layer, results from electron trapping in these blocking layers during discharge. Vinyl Hydroxy ester or vinyl hydroxy amide polymer blocking layers possess extensive hydroxyl-hydroxyl H-bonding which structurally resembles water in its H-bonded state. It is presumed that photodischarged electrons migrate through the hydroxy ester or hydroxy amide vinyl polymer blocking layer medium (plus the small amount of H-bonded water contained therein) much like electrons migrate through water. Thus, when P(4VPy) H-bonds to hydroxyl groups in the P(4VPy)-P(HEMA) blocking layers, many of the hydroxyl-hydroxyl H-bonding sites are disrupted. This decreased hydroxyl-hydroxyl H-bonding density results in blocking layer areas deficient in electron transport capability and electron trapping results contributing to the V_R cycle-up. Thus, the V_R cycle-up is about twice as large in the mixed P(4VPy)-P(HEMA) blocking layer devices (IIe-IIg) versus the layered devices (IIa-IIb). The charge-erase cycling data were obtained at ambient RH using the ambient scanner for 12000 cycles.

TABLE B

Device No.	Conductive Layer	Adhesive-Blocking Layer(s) Composition	Adhesive-Blocking Layer(s) Thickness (micrometer)	$\underline{V}_{0(1)}$	$\underline{V}_{0(12K)}$	$\underline{V}_{R(1)}$	$\underline{V}_{R(12K)}$
IIa	Carboset® 514A	P(4PVPy)-P(HEMA)	0 8-1.0 @ layer	1360	1320	70	160

IIb	CIT	P(4PVPy)-P(HEMA)	0.8-1.0 @ layer	1280	1240	56	130
IIc	Carboset® 514A	P(HEMA)	0.8-1.0	1020	680	30	40
IId	CIT	P(HEMA)	0.8-1.0	1200	1180	28	56
IIe	Carboset® 514A	P(4VPy)-P(HEMA) 1:1[a]	0.8-1.0	1440	1600	40	270
IIf	Carboset® 514A	P(4VPy)-P(HEMA) 2:1[a]	0.8-1.0	1200	1440	92	300
IIg	Carboset® 514A	P(4VPy)-P(HEMA) 1:2[a]	0.8-1.0	1360	1600	48	290

a) Repeat unit molar ratios: The repeat unit molar ratio is the weight in grams of each polymer in the polymer blend corresponding to the product of a constant (any positive number) times the molecular weight of the repeat unit of each polymer. The molecular weight of the repeat unit of each polymer is calculated in the same manner as molecular weights for non-polymeric materials. The polymeric repeat unit molecular weight is the product of the atomic weight of each atom in the repeat unit times the number of atoms summed for all the atoms in the repeat unit. The repeat unit molecular formulae for P(HEMA) and P(4VPy) are $C_6H_{10}O_3$ and C_7H_7N, and the repeat unit molecular weights are 130.15 and 105.14 respectively.

The Carboset 514A conductive layers on Tedlar® substrates were drawbar coated for devices IIa and IIc and were spray coated for devices IIe-IIg. The formulations, coating conditions and drying conditions for both fabrication methods were described in Example I. The as received carbon impregnated Tedlar® (CIT) bulk conductive substrates were drawbar coated with the P(HEMA) blocking layer solution.

In devices IIa-IId, with blocking layers containing only one polymer, the P(HEMA) (0.6 gram) was coated from a 6 weight percent solution in methanol (9.4 grams). The same formulation was used to coat the thick P(4VPy) adhesive layer in devices IIa and IIb and a 0.5 mil drawbar gap was used for both layers. Standard drying conditions were employed for both layers wherein standard drying conditions are one hour at ambient conditions and one hour at 100°C in an air convection oven. The P(HEMA) used in the above TABLE B was obtain from Polysciences, Inc. (see Example IV) and the P(4VPy) from the Reilly Tar & Chemical Co. as Reillene® 4200.

For devices (IIe-IIg) containing both P(HEMA) and P(4VPy) as a mixed polymer blocking layer composition, approximately 6 weight percent solutions of the combined polymers were prepared in 90:10 (by weight) of 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoroisopropanol. Both polymers dissolved in the acidic alcohol mixture whereas a non-coatable gummy precipitate formed in methanol thus precluding non-fluorinated alcohols as coating solvents. Standard blocking layer drawbar gap (0.5 mil) and drying conditions (as defined above) were employed. The compositions of the coating solutions are described in the following TABLE C.

TABLE C

Device No.	REPEAT UNIT MOLAR RATIO P(4VPy)		REPEAT UNIT MOLAR RATIO P(HEMA)	P(4VPy) m Mole	P(4VPy) Grams	P(HEMA) m Mole	P(HEMA) Grams
IIe[a]	1	:	1	5.00	0.65	5.00	0.53
IIf[a]	2	:	1	6.93	0.73	3.47	0.45
IIg[a]	1	:	2	3.23	0.34	6.46	0.84

a) Solutions were prepared in 16.68 grams trifluoroethanol and 1.86 grams hexafluoroisopropanol.

In order to identify a useful blocking layer thickness window, it was necessary to obtain a coating solution concentration versus dry coating thickness relationship for the blocking layer polymers and adhesive layer polymers when using a 0.5 mil drawbar gap to coat these layers. The blocking layer polymer, poly(2-hydroxypropylmethacryate) P(HPMA), was coated onto smooth 2" x 2" glass substrates from a 90:10 by weight solvent mixture of isobutanol:isopropanol at four concentrations, 1.2, 3.6, 6.0 and 8.4 weight percent, after drying as described above (standard conditions) and the dry thickness of the coatings was measured with a Dektak® surfaceprofile measuring system. The Dektak® is available from Sloan Technology Corp. (Model #900050) and uses a hemispherical diamond stylus of 0.0001" radius to make the measurement. This instrument measures thickness by drawing the stylus over the coated surface and then off the coated edge onto the high tolerance uncoated smooth glass (Corning #7059) surface. The vertical step from the coated surface to the smooth glass surface is simultaneously amplified and recorded on thickness calibrated graph paper enabling rapid measurement of the step and thus the thickness. Dektak® steps were measured at four different surface locations in each of three coatings made from a given concentration of P(HPMA). For a given coating, a 2-6 percent thickness variation was found, and the thickness variation among the three coatings made from the same concentration of P(HPMA) was always less than 10 percent. These measurements enabled coating thickness ranges as indicated in Example I and the above table, and in all subsequent tables of this embodiment. Using the P(HPMA) dry coating thickness versus concentration curve for other amorphous organic polymers and copolymers, coated from sufficiently viscous solutions which totally fill the 0.5 mil drawbar gap, is a valid extension of the correlation because these polymers have similar densities. Thus, the thickness will reside within the cited ranges.

To further illustrate the effect of increasing P(4VPy) thickness on V_R cycle-up, the P(4VPy) adhesive layer thickness was systematically increased on top of a P(HEMA) blocking layer of constant (0.8-1.0 micrometer) thickness. The P(HEMA) used in this segment of this Example was the very high molecular weight variety available from Scientific Polymer Products, Inc. (Example IV) which was coated and dried as described above for the lower molecular weight P(HEMA). Instead of formulating the blocking layer solution in methanol, Dowanol® PM was used as the coating solvent again at 6 weight percent as previously described. Dowanol® PM, available from Dow Chemical Co., is a glycol methyl ether systematically named as 1-methoxy-2-hydroxypropane.

The P(4VPy) adhesive layers were coated and dried as previously described in Example I formulated in the 90:10 by weight isobutanol:isopropanol solvent mixture. The dry P(4VPy) thicknesses were estimated from the Dektak® generated P(HPMA) calibration curve. For concentrations less than 1.2 weight percent and greater than 8.4 weight percent, thicknesses were estimated from the Dektak® curve extrapolated at either end. Thus, P(4VPy) concentrations of 0.0, 0.3, 0.6, 1.2, 2.5, 5.0 and 10.0 weight percent correspond to the estimated adhesive layer thicknesses in the following table. The precise thickness of the P(4VPy) adhesive layer is unimportant so long as the coating concentration and drawbar gap can be correlated to an electrically useful charge-erase window. The bulk conductive substrate, carbon impregnated Tedlar (CIT), was used for all the devices in this adhesive layer thickness study. All devices electrically tested in this Example (both tables) contain charge generator and transport layers formulated, coated and dried as described in Example I. The charge-erase cycling data in the following table were obtained at ambient RH using the environmental scanner for 200 cycles.

TABLE D

Device No.	P(4VPy) Adhesive Layer (Approx. thickness) (micrometer)	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
IIh	0.0	1095	1115	55	50
IIi	0.03	880	890	40	40
IIj	0.06	925	935	40	40
IIk	0.12	940	975	45	50
III	0.25	1090	1120	55	65
IIm	0.50	875	950	50	70
IIn	1.00	945	1045	70	95

The above data in TABLE D indicates a V_R cycle-up in 200 cycles starting at about 0.25 micrometer P-(4VPy) which corresponds to a coating solution concentration of 2.5 weight percent. The V_R cycle-up ($V_{R(200)}$ - $V_{R(1)}$) becomes progressively larger (from 10 to 25 volts) with increasing P(4VPy) thickness. Adhesive layer thicknesses between 0.03 and 0.12 micrometer, corresponding to a P(4VPy) concentration range of 0.3 to 1.2 weight percent, provide a useful adhesive layer thickness window wherein sufficient adhesion is provided for routine handling without delamination, and acceptable charge-erase cycling data is obtained.

The initial charge acceptance, which is maintained in all devices for 200 cycles and in most of the devices for 12000 cycles, indicates the 0.8-1.0 micrometer P(HEMA) hole blocking layer is minimizing charge injection from the carbon based conductive layers. The latter charge at a much lower level (Example I) when the blocking layer is omitted in an otherwise identical device.

EXAMPLE III

This example illustrates the use of P(4VPy) and P(2VPy), available from Reilly Tar & Chemical Co. as Reillane® 4200 and 2200 respectively, as a combined hole blocking and adhesive layer in an attempt to eliminate the need for a vinyl hydroxy ester or vinyl hydroxy amide polymer blocking layer. This Example will first describe a device set in which all the layers were drawbar coated, and then a second device set in which all the layers were spray coated. Both device sets were fabricated on carbon black conductive layers but in the second set a metallic conductive layer (titanized Mylar) was also included to evaluate the impact of the conductive layer on charge-erase electrical performance. The adhesive/blocking layers of the first device set were formulated, drawbar coated and dried as described in the following table.

TABLE E

Device No.	Conductive Layer[a] Tedlar Substrates	Adhesive/Blocking Layer Formulations Weight % P(VPy) (micro meter)[b]	Grams P(VPy)	Grams Solvent(s)
IIIa[c]	CIT	6 (0.8-1.0)	0.3 P(4VPy) + 0.3 P(2VPy)	5.64 isopropanol + 3.76 isobutanol
IIIb[d]	CIT	1.5	0.15 P(4VPy) +	9.85 t-butanol
		1.5 (0.20 - .25 each)	0.15 P(2VPy)	5.91 isopropanol + 3.94 isobutanol
IIIc[c]	Carboset 514A	6 (0.8 - 1.0)	0.3 P(4VPy) + 0.3 P(2VPy)	5.64 isopropanol + 3.76 isobutanol
IIId[d]	Carboset 514A	1.5	0.15 P(4VPy)	9.85 t-butanol
		1.5 (0.20 - .25 each)	0.15 P(2VPy)	5.91 isopropanol + 3.94 isobutanol

a) Conductive layers & Carboset drawbar procedure described in Example I
b) Thicknesses based on Dektak™ measurement (Example II) and all coatings fabricated with 0.5 mil gap and dried using standard conditions.
c) One adhesive/blocking layer coating from combined polymer solution.
d) P(4VPy) adhesive blocking layer coated over P(2VPy) blocking layer from two polymer solutions.

After coating the above adhesive/blocking layers, the devices were completed by sequentially drawbar coating the charge generator and transport layers; the formulation, coating and drying conditions for which were described in Example I.

Charge-erase electrical cycling of the completed devices was effected at ambient RH using the ambient cyclic scanner for 12,000 cycles

TABLE F

Device No	Conductive Layer	Adhesive/Blocking Layers Composition/Thickness[a]	$V_{O(1)}$	$V_{O(12K)}$	$V_{R(1)}$	$V_{R(12K)}$
IIIa	CIT	P(4VPy) - P(2VPy) 0.8 - 1.0	1240	1320	110	305
IIIb	CIT	P(4VPy) / P(2VPy) 0.20 - .25 each	1220	1110	80	200
IIIc	Carboset 514A	P(4VPy) - P(2VPy) 0.8 - 1.0	1160	1200	75	180
IIId	Carboset 514A	P(4VPy). / P(2VPy) 0.20 - .25 each	700	800	40	150

[a])Thicknesses in micrometers.

The V_R cycle-up observed for all four devices indicates devices IIIb and IIId, which were intended to have a layered structure of poly(vinylpyridine) isomers, in fact, have mixed significantly. Apparent the initially layered structures in IIIb and IIId mix extensively during coating of the charge transport layer from methylene chloride which is a solvent for both isomers In addition, the THF used to coat the charge generator layer may channel through the top P(4VPy) layer to dissolve the underlying P(2VPy) which would promote interlayer mixing between the two P(VPy) layers and also between the P(VPy) layers and the PVK generator layer binder. Since the P(2VPy) isomer is soluble in both methylene chloride and THF and the P-(4VPy) isomer is soluble only in methylene chloride, it is very likely that the more soluble P(2VPy) migrates upward into the charge generator and transport layers more extensively than does the P(4VPy) isomer. Thus, the V_R cycle-up reflects the presence of hole trapping P(2VPy) in the charge active layers.

Although the vinyl hydroxy ester or vinyl hydroxy amide polymer is not necessary to prevent conductive layer hole injection in these mixed P(VPy) isomer blocking layer devices (V_o values are large), its presence is necessary to help anchor the P(VPy) isomers through hydrogen bonding to the P(HEMA) hydroxyl groups. This anchoring reduces or substantially eliminates [when a thin layer of P(VPy) isomer is used] hole trapping P(VPy) migration into the charge active layers during coating thereof and so V_R cycle-up decreases. The P(4VPy) anchoring mechanism by P(HEMA) is described in Example II and also applies to P(2VPy), but probably to a lesser extent because H-bonding to P(2VPy) is more sterically hindered than to P(4VPy). Thus, the P(2VPy) is more free to migrate during coating than is the P(4VPy) because of solubility and H-bonding considerations.

The totally sprayed second device set of this Example will next be described. The Carboset 514A carbon black conductive layer was formulated, spray fabricated onto Mylar and dried as described in Example I, and the titanized Mylar was used as received from E.I. duPont de Nemours & Co. These substrate-conductive layers were next spray coated with a dilute solution (0.9 weight percent) of either P-(VPy) isomer in mixed alcohol solvents. The spray solution was formulated by mixing 6.86 grams of P-(4VPy) or P(2VPy) with 663.6 grams isobutanol and 79.6 grams isopropanol in an amber quart bottle which was roll milled for 2-5 hours to obtain a solution. This blocking layer solution was sprayed using commercially available spray guns and equipment manufactured by Binks Manufacturing Co. The Sinks Model 21 automatic spray gun was used in the Sinks spray booth Model BF-4 with a type 42753 reciprocator. The Model 21 gun was equipped with a 63B fluid nozzle and a 63PE air atomization nozzle The fluid pressure was 4 psi and the spray atomization pressure was 55 psi. The needle setting was at 0.75 turns and the spray fan angle at 0.50 turns counted from the closed position. The spray gun was operated in an automatic mode and was traversed on a reciprocator while spraying from the top to the bottom of the vertically placed mandrel. The substrate-conductive layer sheets to be sprayed were tape mounted and rotated on a cylindrical aluminum mandrel positioned on a shaft connected to a turntable. The blocking layers solution was spray cycled with two or four passes with 1.5 minutes elapsing between passes. Finally, the coating was removed from the mandrel and was dried at 120° C for 5 minutes in an air convection oven.

The dry thickness of these sprayed P(VPy) blocking layers, although not measured, is estimated for the two pass layer to be between 0.5 to 1.5 micrometer and for the four pass blocking layer to be between 1.5 to 2.5 micrometer.

The generator layer mixture was then formulated for spray fabrication using the masterbatch formulation described in Example I. To 200 grams of the generator layer masterbatch in a one quart amber glass bottle was added 258 grams of toluene and 258 grams of THF and this mixture was magnetically stirred for 3-4 hours prior to spray coating. The dispersion (3.65 weight percent total solids) was sprayed using the previously described Binks equipment. The fluid pressure was 4 psi and the spray atomization pressure was 55 psi. The needle setting was at 0.75 turns and the spray fan angle at 0.5 turns counted from the closed position. The spray gun was operated in an automatic mode and was traversed on a reciprocator while spraying from the top to bottom of the vertically placed mandrel. The partially fabricated devices consisting of a substrate, conductive layer and blocking layer were tape mounted and rotated on a cylindrical aluminum mandrel positioned on a shaft connected to a turntable. The generator layer dispersion was spray cycled in three passes with 1.5 minutes elapsing between passes. Finally, the coating was removed from the mandrel and was dried at 120°C for 5 minutes in an air convection oven. The generator layer dry thickness was estimated to be between 0.4 and 2.0 micrometers in thickness.

Finally, the charge transport layer composition was formulated and sprayed. A one gallon amber glass bottle was charged with 88 grams N,N'bis-(3"-methylphenyl)-[1,1'-biphenyl]-4,4'diamine, 132 grams polycarbonate resin (Merlon M-39, available from Mobay Chemical Co., Inc.), 2640 grams of methylene chloride and 1760 grams of l,l,2-trichloroethane. After roll milling the bottle for two days, the resulting solution was sampled for spray fabrication using the previously described spray equipment manufacture by Binks Manufacturing Co. The fluid pressure was 8 psi and the spray atomization pressure was 55 psi. The needle setting was at 0.75 turns and the spray fan angle at 0.5 turns counted from the closed position. The spray gun was operated in an automatic mode and was traversed on a reciprocator while spraying from the top to the bottom of the vertically placed mandrel. The partial devices with the last coated generator layer on the surface were tape mounted and rotated on a cylindrical aluminum mandrel position on a shaft connected to a turntable. The above transport layer solution was sprayed in five passes with 1.5 minutes elapsing between passes. Finally, the coating was removed from the mandrel and was dried at 120°C for 10 minutes in an air convection oven. The transport layer dry thickness was found to be between 20-30 micrometers using the previously described Dektak® (Example II) procedure.

The above devices, totally sprayed except for the substrate and the two commercially available titanized Mylar substrate-conductive layer combinations, were charge-erase cycled for 200 cycles at ambient RH using the ambient scanner. The electrical cyclic results are indicated in the following table.

TABLE G

Device No.	Conductive Layer	Polymer Blocking Layer	$V_{O(1)}$[c]	$V_{O(2\text{-}5)}$[d]	$V_{O(200)}$[e]	$V_{R(1)}$[f]	$V_{R(200)}$[f]
IIIe	Carboset 514A	P(4VPy)[a]	700	360_4	400	45	30
IIIf	Carboset 514A	P(4VPy)[b]	750	450_5	500	45	70
IIIg	Titanium	P(4VPy)[a]	800	820_2	720	35	50
IIIh	Carboset 514A	P(2VPy)[a]	660	550_2	600	100	180
IIIi	Carboset 514A	P(2VPy)[b]	640	500_2	560	70	140
IIIj	Titanium	P(2VPy)[a]	820	880_2	920	80	225

a) Blocking layer thickness close to 1.0 micrometer (1.0 ± 0.3).

b) Blocking layer thickness close to 2.0 micrometers (2.0 ± 0.3).

c) $V_{O(I)}$ is the initially measured surface voltage directly after corotron charging the device the first time.

d) $V_{O(2\text{-}5)}$ is the measured surface voltage obtained after corotron charging and photodischarging the device for 1 or 2 or 3 or 4 cycles and charging for the 2nd, 3rd, 4th or 5th cycle, respectively.

e) $V_{O(200)}$ is the surface voltage measured after corotron charging and photodischarging the device for 199 cycles and charging for the 200th cycle.

f) V_R is the residual voltage after corotron charging and photodischarging the device for the indicated number of cycles.

The P(VPy) blocking layers in these carbon black conductive layer devices have inferior blocking capability compared to other blocking layers containing vinyl hydroxy ester polymers alone (IIc & IId), vinyl hydroxy ester polymers with P(4VPy) adhesive layers (IIa & IIb), and mixed P(VPy) isomers without vinyl hydroxy ester polymers present (IIIa-IIId). The improved blocking capability (higher V_o versus the same devices without a blocking layer in Example I) of the aforementioned three blocking layer compositions indicates these compositions are more effective in preventing conductive layer components from mixing upward into the generator and/or transport layers during coating of these layer. The solvent barrier properties of these compositions contribute significantly to blocking conductive layer mixing and its effect, i.e. decreased V_O with cycling. P(4VPy) and P(2VPy) blocking layers alone (devices IIIe, IIIf, IIIh, IIIi) have insufficient solvent barrier properties to subsequently applied coating compositions which leads to V_O charge depletion levels just above that found in the Example I devices (no blocking layers) having the same conductive layer. The rapid (2-5 cycles) V_O cycle-down in the above devices (TABLE G) dictates the severity of the interlayer mixing and V_O charge depletion. The absence of the possibility of conductive layer component mixing in the titanium conductive layer devices (IIIg & j) appears electrically as higher $V_{O(1)}$ with retention thereof with cycling. The presence of the natural titanium oxide blocking layer on this metallic conductive layer also contributes to the prevention of V_O cycle-down. The absence of V_O cycle-down in the titanium devices provides indirect evidence that carbon black conductive layers are deleteriously involved in causing V_O

cycle-down in otherwise identical devices.

The V_R cycle-up in the device set of the above TABLE G occurs extensively in all the P(2VPy) blocking layers devices (IIIh-IIIj) independent of conductive layer composition. The most likely cause of V_R cycle-up originates in the ease of P(2VPy) migration into the generator and/or transport layers during solvent coating of these layers. As a result, hole trapping occurs with V_R cycle-up similar to that observed in drawbar coated devices (IIIa-IIId) which also contain P(2VPy). The absence of extensive V_R cycle-up in the P(4VPy) blocking layer devices (IIIe-IIIg) may reflect a lesser degree of P(4VPy) migration into the upper (CGL, CTL) layers during coating thereof. In addition, the P(4VPy) is not as effective a hole trapping material as is the P(2VPy), so migrated P(4VPy) is less effective than migrated P(2VPy) in forming trap sites. The V_R in IIIe-IIIg therefore cycles up much less. Since none of the devices in this Example delaminated during routine fabrication and electrical testing procedures, the interfacial adhesion at all interfaces is sufficient to enable photoreceptor use. Overall, the electrical cycling properties of the devices in this Example illustrate two important desirable properties of a photoreceptor blocking layer: (1) The blocking layer should co-function, as much as possible, as a barrier layer to subsequently applied coating compositions so that it becomes a protective coating for non-metallic conductive layers. (2) The blocking layer itself should be insoluble in subsequently applied coating compositions so that it can maintain barrier properties [as described in (1)] and so that the blocking layer material itself does not migrate into the CGL and CTL during coating thereof. The insolubility of the vinyl hydroxy ester or vinyl hydroxy amide polymer blocking layers of this application arises from dense intermolecular hydrogen bonding.

EXAMPLE IV

In this Example, the use of three different molecular weights of poly(2-hydroxyethylmethacrylate) P-(HEMA) as a blocking layer on the conductive substrate, carbon impregnated Tedlar® (CIT), is illustrated. Polymers were obtained from three different sources and were characterized by intrinsic viscosity. Weight average molecular weight was determined only for the highest viscosity polymers using a standard light scattering method. The intrinsic viscosity $[\eta]$ was measured in methanol solution at 25° C by extrapolation to infinite dilution of reduced viscosities obtained at four different concentrations (% g/dl) 1.0, 0.67, 0.50 and 0.40. A trace of insoluble polymer was first filtered from the Polyscience sample but the other two samples were totally soluble in methanol. The data are summarized in the following table.

TABLE H

Source of P(HEMA)	$[\eta]$dl/g	$\overline{Mw}$
Scientific Polymer Products	0.654	1.0-1.4 x 10^6
Polyscience	0.506	---
Synthesized	0.272	---

The glass transition temperature for the 0.654 intrinsic viscosity P(HEMA) was found to be 110° C by DSC. This value decreases considerably, as a function of residual solvent and undefined thermal histories, in various P(HEMA) samples. Glass transition values for P(HEMA) have been reported in a temperature range of 55° C-104° C. [L.R. Brostrom, D.L. Coleman, D.E. Gregonis and J.D. Andrade, Makromol. Chem., Rapid Commun. 1, 341-343 (1980).]

NMR analysis (C^{13}) of the 0.654 intrinsic viscosity P(HEMA) in concentrated (7-8 weight percent) DMSO-d_6 solution between 297° K- 307° K provided information concerning the tacticity of the polymer. The NMR spectrometer was a Bruker AM 360 equipped with a 5 mm QNP probe at a carbon frequency of 90.5 MHz. The C_{13} spectrum was obtained using inverse grated decoupling with 30 seconds recycle delay between acquisitions to ensure quantitative integrals for all carbon nuclei. Monitoring the alpha-methyl carbon signal area indicated the following percent triad repeat unit content: 67 percent syndiotactic, 30 percent heterotactic and 3 percent isotactic. P(HEMA) tacticities were previously studied using C_{13}-NMR wherein P(HEMA) obtained from a radical solution polymerization had a similar triad distribution, i.e. 58 percent syndiotactic, 42 percent heterotactic <1 percent isotactic [D.E. Gregonis, G.A. Russell, J.D. Andrade and A.C. deVisser, Polymer 19, 1279-1284 (1978)]. Thus, the triad content for the 0.654 intrinsic viscosity P-(HEMA) is typical of a radically polymerized polymer.

The low molecular weight P(HEMA) was prepared using a modification of the procedure described in a Czechoslovakian Patent [Chem. Abstr. 99(2): 14003j (1982); Czech CS200433B, No. 30, 1982] wherein the solvent was changed from methyl Cellosolve to tertiary butylalcohol and the crosslinking agent was omitted. More specifically, to a 500 ml three neck round bottom flask, equipped with an air reflux condenser, an argon inlet and outlet, a heating mantle as heat source and a magnetic stirring football for magnetic stirring was charged 40 grams of Mhoromer BM-920 (available from Rohm Tech, Inc.) which is 2-hydroxyethylmethacrylate or HEMA monomer. The monomer was first passed three times through a De-Hibit 100 (Polysciences Inc.) ion exchange resin column (24" x 1" diameter column) to remove the 200 ppm methylhydroquinone polymerization inhibitor. To the flask was also charged 240 grams of tertiary butylalcohol (99.5 percent purity, available from Aldrich Chemical) and 0.159 grams AIBN (Polysciences, Inc.) polymerization initiator, which is 0.3 mole percent based on the monomer charge. The solution was magnetically agitated and argon gas was passed through the solution throughout the polymerization period. The solution was heated at gentle reflux (79°C) for 16 hours, was cooled to ambient temperature, and the viscous polymer solution was coagulated into 3.2 l of reagent grade toluene. The coagulated polymer was vacuum filtered on a coarse frit funnel and the filtered polymer was slurried at room temperature with 300 ml reagent grade tetrahydrofuran. The slurried polymer was filtered as before and dried overnight in a vacuum oven on a sheet of Mylar at 60°C at 0.5 mm Hg. The dried water-white polymer yield was 31 .25g (78.1 percent of theory) and had an intrinsic viscosity of 0.272 dl/g. This material was used without further purification to drawbar coat blocking layers.

In the first electrical data set shown in TABLE I below, the low molecular weight P(HEMA) is compared to the moderate molecular weight P(HEMA), $[\eta]$ = 0.272 vs. 0.506 dl/g. All devices were drawbar (0.5 mil gap) fabricated on the bulk conductive substrate, carbon impregnated Tedlar® (CIT). The blocking layer compositions were formulated as follows.

TABLE I

Device No.	P(HEMA) Solids Level (Weight %)	P(HEMA) (Grams)	Solvent Type	Solvent Grams
IVa	3.6	0.36	methanol	9.64
IVb	6.0	0.60	methanol	9.40
IVc	3.6	0.36	t-butanol	9.64
IVd	7.2	0.72	t-butanol	9.28

After drying the coated blocking layers at standard conditions (Example II), devices IVc and IVd were further coated with a 0.6 weight percent solution of P(4VPy) as described in Examples I and II. Charge generator and transport layers were formulated, coated and dried as described in Example I. The devices were electrically charge-erase evaluated at ambient RH (= 12 percent) and low RH (<5%) as indicated in the following table.

TABLE J

Device No.	P(HEMA) [η] (dl/g)	Blocking Layer Thickness (micrometer)	%RH	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
IVa^a	0.272	0.5-0.7	12	910	800	25	32
IVb^a	0.272	0.8-1.0	12	890	870	28	57
IVc^b	0.506	0.5-0.7	29	1400	1420	45	50
IVd^b	0.506	0.5-0.7	<5	1340	1360	60	80
IVd^b	0.506	1.0-1.2	29	1380	1410	40	50
IVd^b	0.506	1.0-1.2	<5	1320	1360	55	75

a) Data obtained on the ambient cyclic scanner.

b) Data obtained on the environmental cyclic scanner.

The $V_{O(1)}$ data and $V_{O(200)}$ data indicate surface charge retention thereby showing that both P(HEMA) samples block hole injection in the thickness range 0.5 to 1.2 micrometers and in the RH range <5-29 percent. The very low humidities (<5% RH) cause a slight increase in V_R and V_R cycle-up in 200 cycles. The presence of the 4-PVPy adhesive layer seems to have little effect on cyclic electrical properties.

In the second set of charge-erase electrical data in TABLE L below, high molecular weight ([η] =0.654dl/g) P(HEMA) was evaluated as a drawbar fabricated blocking layer on the same bulk conductive substrate, carbon impregnated Tedlar (CIT). P(HEMA) methanol solutions of 1.8, 3.6, 6.0 and 14.4 weight percent were formulated coated and dried as described in the first data of this Example. When a P(4VPy) adhesive layer was used, it was formulated, coated and dried as described in Examples I and II for the 0.6 weight percent coating solution. Charge generator and charge transport layers were formulated, coated and dried as described in Example I. The devices were evaluated at ambient (27 %) and low (<5%) relative humidities using the ambient cyclic scanner. The presence or absence of a 0.06 micrometer P(4VPy) adhesive layer (thickness projected as described in Example II) in the following table is noted with a yes or no. Blocking layer thicknesses were obtained from the Dektak generated calibration curve In Example II.

TABLE K

Device No	P(4VPy)	Blocking Layer (micrometer)	%RH	$V_{O(1)}$	$V_{O(20)}$	$V_{O(200)}$	$V_{O(c4K)}$	$V_{R(1)}$	$V_{R(20)}$	$V_{R(200)}$	$V_{R(c4K)}$
IVe	No	0.2-0.4	27	920	860	800	800	22	20	20	25

IVe	No	0.2-0.4	<5	840	800	800	800	30	35	35	35
IVf	Yes	0.2-0.4	27	1030	980	960	960	32	30	30	40
IVf	Yes	0.2-0.4	<5	900	760	760	760	45	50	50	50
IVg	No	0.5-0.7	27	880	900	880	920	25	25	25	30
IVg	No	0.5-0.7	<5	840	860	860	880	37	65	65	55
IVl	Yes	0.5-0.7	27	1000	980	980	1000	25	25	25	27
IVl	Yes	0.5-0.7	<5	920	980	980	940	37	57	57	45
IVm	No	0.8-1.0	27	940	960	960	980	25	25	20	20
IVm	No	0.8-1.0	<5	940	1000	1000	1020	30	40	50	50
IVn	Yes	0.8-1.0	27	940	1000	1020	1050	25	30	25	22
IVn	Yes	0.8-1.0	<5	960	1050	1050	1050	35	75	80	70
IVo	No	2.0-2.4	27	800	880	880	800	75	90	95	115
IVo	No	2.0-2.4	<5	840	1050	1070	950	100	180	210	200
IVp	Yes	2.0-2.4	27	800	960	960	1020	180	220	230	320
IVp	Yes	2.0-2.4	<5	860	1100	1100	1020	205	270	300	280

All devices, in the Table K immediately above, adequately prevented hole injection as evidenced by high $V_{O(1)}$ and retention thereof out to $V_{O(4K)}$. In the blocking layer thickness range of 0.2 to 1.0 micrometer, generally acceptable V_R and V_R cycle-up were observed in this 4000 cycle test at both low and ambient RH. However, depending upon the specific conductive layer composition employed, blocking layer thicknesses of greater than about 2 micrometers may be too thick to enable complete photodischarge (V_R cycle-up) at ambient or low RH in the presence or absence of an adhesive layer. The presence of an adhesive layer in the 0.2 - 1.0 micrometer range is electrically negligible except at 1.0 micrometer where a significant V_R cycle-up at low RH (35 to 70 volts) occurred in 4,000 cycles. Thus, when using the P(4VPy) adhesive layer, blocking layer thickness of 0.2 - 0.7 micrometer are favored in that the V_R increase at low RH is considerably less. Thus, all three of the above P(HEMA) samples provide useful hole blocking capacity on chemically inert CIT conductive layers.

EXAMPLE V

Illustrated in this Example is the use of two different molecular weights of P(HEMA) as blocking layers on a conductive polypyrrole based polymer (ICP-117 from Polaroid Corp.). The conductive polymer dispersion was formulated, drawbar coated and dried as described in Example I on either insulative polymer substrates, Mylar or Tedlar®. The P(HEMA) blocking layer solution were prepared with three coating solvents using a 0.5 mil bar gap unless otherwise indicated. Thicknesses for methanol and Dowanol PM coated P(HEMA) blocking layers were projected from the dry thickness/concentration curve described in Example II for P(HEMA). For t-butanol coated P(HEMA) blocking layers, a 2 weight percent solution was coated since the highest molecular weight P(HEMA) failed to dissolve in this particular solvent at higher ambient concentrations. Larger drawbar gaps were used in an attempt to increase the blocking layer thickness which was estimated at 0.2 - 0.4 micrometer for P(HEMA) blocking layers coated from t-butanol. Standard drying conditions (Example II) were employed for all the P(HEMA) blocking layer compositions irrespective of coating solvent. The P(HEMA) blocking layer compositions in methanol or Dowanol PM were formulated at 3.6 and 6.0 weight percent to give projected dry thicknesses of 0.5 to 0.7 and 0.8 to 1.0 micrometer, respectively. Since no P(4VPy) adhesive layers were used, the charge generator and transport layers were next formulated, drawbar coated and dried as described in Example I. All charge-erase cycling data were obtained at ambient RH (12-29 percent) using the cyclic scanners indicated in the following TABLE L.

TABLE L

Device No.	$[\eta]$	P(HEMA) Blocking Layer Solvent	P(HEMA) Blocking Layer Thickness (μm)	%RH	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
Va	0.272	Methanol	0.5-0.7	12	400	380	18	48
Vb	0.272	Methanol	0.8-1.0	12	380	340	15	25
Vc	0.654	Methanol	0.5-0.7	16	600	560	29	82
Vc	0.654	Methanol	0.5-0.7	29	630	650^a	55	205^a
Vd	0.654	Methanol	0.8-1.0	16	770	780	20	20
Vd	0.654	Methanol	0.8-1.0	29	780	790^a	20	45^a
Ve	0.654	t-Butanol	0.2-0.4^b	15	400	410	26	50
Vf	0.654	t-Butanol	0.2-0.4^c	15	440	460	26	55
Vg^d	0.654	Dowanol PM	0.8-1.0	21	805	860	30	50
Vh^d	0.654	Dowanol PM	0.5-0.7	21	385	450	40	105

[a] 3,500 continuous cycles.

[b] 2 weight percent solution using a 1 mil bar gap.

[c] 2 weight percent solution using a 1.5 mil bar gap.

[d] Environmental cyclic scanner used for this device and the ambient cyclic scanner used for the other devices in the table.

Inspection of the above charge-erase cycling data reveals several facts pertinent to the P(HEMA) molecular weight and blocking layer thickness when applied over the ICP-117 conductive layers. The lower molecular weight P(HEMA) blocking layers at both thicknesses were ineffective in obtaining high V_O values desirable in xerographic photoreceptors. Because lower molecular weight P(HEMA) is a poorer solvent barrier, the solvent used in coating the CGL and CTL readily mixed with the conductive layer components causing them to migrate upwards into the CGL and/or the CTL. Once out of their intended location, migrated conductive layer components deplete charging and give rise to the low V_O (devices Va and Vb). Devices (Vd and Vg) containing 0.8 - 1.0 micrometer of high molecular weight P(HEMA) blocking layers afford xerographically useful high V_O values confirming the strong solvent barrier properties attributable to high molecular weight P(HEMA). However, as the thickness of the high molecular weight P(HEMA) was reduced to 0.5 - 0.7 micrometer in devices Vc and Vh, V_O values decreased indicating even the high molecular weight P(HEMA) blocking layer, when less than about 0.8 micrometer, is not as strong a solvent barrier on ICP- 177 conductive layers as compared to its effectiveness as a barrier on chemically inert CIT conductive layers. This conductive layer composition has an aggressive affinity for subsequently used organic coating solvents. This implies that a very low level of organic solvent penetration through the high molecular weight P(HEMA) blocking layer is sufficient to generate extensive mixing and upward migration of charge depleting conductive layer components. In contrast, as little as 0.2 micrometer of high molecular weight P(HEMA) was sufficient to achieve and retain high V_O values in 4,000 cycles when coated on the solvent inert bulk conductive substrate, carbon impregnated Tedlar® (CIT) (devices IVe and f in Example IV). Thus, the more solvent inert a conductive layer is, the less stringent are the solvent barrier requirements of the blocking layer, thus enabling the use of thinner blocking layers. There appears to be no blocking layer coating solvent effect on electrical properties when sufficiently thick (0.8-1.0 micrometer) blocking layers are coated. This suggests both coating solvent, Dowanol PM and methanol are effectively removed in convection oven drying, and also that the two solvents do not alter the intermolecular H-bonding density by altering the bulk morphology of the P(HEMA). Since only thin blocking layers could be coated from the t-butanol/P(HEMA) solutions, any solvent effect on electrical properties will be masked by the already discussed conductive layer mixing problem.

The V_R cycle-up in devices Vc and Vh implies a charge trapping mechanism is simultaneously operative with the charge depletion mechanism. The precise cause of the trapping mechanism is unclear, but it is possible that some of the P(HEMA) is moved up into the CGL and/or CTL during coating thereof. As conductive layer components migrate up through the P(HEMA) blocking layer into the CGL and CTL, some of the P(HEMA) may be uprooted and carried along into these layers resulting in charge trapping and the observed V_R cycle-up.

EXAMPLE VI

The first device set of this Example illustrates the use of poly(2-hydroxypropylmethacrylate), P(HPMA), as a blocking layer on the carbon based conductive layer crosslinked Carboset 514. Tedlar® substrates were used for all four devices wherein devices VIa, VIb and VId contained spray coated conductive layers and device VIc a drawbar coated conductive layer. The Carboset 514A was formulated, coated and dried as described in Example I. The P(HPMA) (available from Polysciences, Inc.) blocking layers were coated (drawbar gap 0.5 mil) from a 90/10 by weight solvent mixture of isobutanol/isopropanol at concentrations of 1.2, 3.6, 6.0 and 8.4 weight percent to give dry coating thicknesses of 0.1-0.3, 0.5-0.7, 0.8-1.0 and 1.3-1.5 micrometers, respectively. The thicknesses were projected from the dry thickness/concentration curve developed for this polymer in Example II. After drying the blocking layer at standard conditions (Example II), a P(4VPy) adhesive layer was coated (drawbar gap 0.5 mil) from 0.4-0.6 weight percent solutions. The adhesive layer solvent composition and drying conditions were the same as used for the blocking layer coating. Charge generator and transport layers were sequentially applied as described in Example I. Charge-erase electrical cycling data were obtained with the ambient cyclic scanner at ambient RH (38-40 percent) for 12,000 cycles. In one case, the device tested for 12,000 cycles was dark rested at least overnight and was then retested for 45,000 continuous cycles.

TABLE M

Device	P(HPMA) Blocking Layer (micrometer)	X Cycles	$V_{O(1)}$	$V_{O(X)}$	$V_{R(1)}$	$V_{R(X)}$
VIa	0.1-0.3	12,000	900	750	76	140
VIb	0.5-0.7	12,000	880	750	56	68
VIc	0.8-1.0	12,000	840	840	40	35
VIc	0.8-1.0	Rest + 45,000	820	540	60	44
VId	1.3-1.5	12,000	740	680	36	68

The V_O (1 and 12,000) obtained in the above blocking layer thickness range, indicates significant blocking of positive charge (hole) injection from the conductive layer at ambient RH prior to photodischarging. In Example I, a similar device without a blocking and adhesive layer charged to a V_O of only 460 volts. Device VIa, having a thin blocking layer, was the only device that showed VR cycle-up. Because Carboset 514 conductive layers are less chemically inert than CIT conductive layers, mixing of conductive components from the Carboset 514 conductive layer into the thin blocking layer disrupts hydroxyl-hydroxyl H-bonding sufficiently to cause photodischarged electron trapping to occur with each successive xerographic cycle and thus V_R cycle-up occurs. Device VIc, having a blocking layer sufficiently thick to prevent interlayer mixing, cycled flat for the first 12,000 cycles and then exhibited a 33 percent V_O cycle-down in the subsequent 45,000 charge-erase cycling test. The magnitude of the V_O cycle-down is common for such a severe cycling test especially with ozone buildup in the non-ventilated scanner chamber. With dark resting for 24 hours, V_O recovered to approximately the same voltage (Vo) as was found prior to the 45,000 cycling test.

In the second device set of this Example, a head to head comparison was made between P(HPMA) and P(HEMA) blocking layers of the same thickness (0.8-1.0 micrometer) at ambient and low RH charge-erase cycling conditions. The conductive layers were prepared from a carbon black dispersed in an olefinic primer (LE16610) available from the Red Spot Paint & Varnish Co. The LE16610 conductive layer on Tedlar® was formulated, sprayed and dried as described in Example I. Both the P(HPMA) and P(HEMA) [η] = 0.506 were obtained from Polysciences, Inc. and were drawbar coated (0.5 mil gap) onto the sprayed conductive layers using 6 weight percent solutions in t-butanol. The medium viscosity P(HEMA), unlike the high viscosity P(HEMA), dissolved in t-butanol at 6 weight percent. After applying standard drying conditions to the blocking layer, P(4VPy) adhesive layer compositions were formulated, coated and dried as previously described in this Example. Both blocking and adhesive layer thicknesses were estimated from the previously described dry thickness concentration curve (Example II). Charge generator and transport layers were formulated, coated and dried as described in Example I. The devices were tested with the ambient cyclic scanner for 200 cycles.

TABLE N

Device No.	Blocking Layer Composition	% RH	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
VIe	P(HPMA)	58	1220	1420	35	60
VIe	P(HPMA)	<5	1440	1510	60	190
VIf	P(HEMA)	35	900	900	40	50
VIf	P(HEMA)	<5	880	940	35	50

In this device set, both P(HPMA) and P(HEMA) provide satisfactory hole blocking capability in 200 cycles at both ambient and low RH. V_O remains significantly higher that same device in Example I without a blocking layer. However, the P(HPMA) blocking layer device develops considerable V_R cycle-up at low RH testing conditions. This V_R cycle-up is probably not related to interlayer mixing because it did not occur at ambient RH when the same device was tested. More likely, the V_R cycle-up is probably related to a decreased water level in P(HPMA) versus P(HEMA) blocking layers. More trapped water, although not a large amount, in P-(HEMA) versus P(HPMA) assists in enhancing the hydrogen bonding density by bridging hydrophobic (low H-bonding density areas) gaps. Also, hydroxyl H-bonding density in P(HEMA) is probably larger than in P-(HPMA) because of methyl steric hindrance to some of the H-bonding sites in P(HPMA). Presumably, the combination of more water and denser H-bonding in P(HEMA) creates less resistive pathways for the transport of photodischarged electrons through these relatively thick blocking layers without significant electron trapping. Thus, V_R remains low at low RH in P(HEMA) blocking layer devices.

EXAMPLE VII

This Example illustrates the use of P(HEMA) blocking layers at two different molecular weights and three different thicknesses. The blocking layers were drawbar coated on LE16610 carbon black conductive layers which were formulated and sprayed (on Tedlar® substrates) and dried as described in Example I. In addition, three of the high molecular weight P(HEMA) devices were crosslinked with glutaraldehyde, added as a 25 weight percent aqueous solution just prior to drawbar coating the blocking layers. Crosslinking then proceeded after solvent evaporation during air convection oven drying of the coating at 120 °C for one hour. The charged molar ratio of glutaraldehyde to P(HEMA) repeat units in the blocking layer coating solution was held constant at 1:3. Each aldehyde group in the glutaraldehyde molecule is capable of crosslinking two P(HEMA) hydroxyl groups through formation of acetal linkages. The simultaneous elimination of water at 120 °C drives the crosslinking reaction in the absence of acidic catalysis. Crosslinking was confirmed to have occurred at the above stoichiometry and curing conditions in a separate experiment in which the crosslinked coating, which as scraped from a glass slide, was totally insoluble in Dowanol PM. The P-(HEMA) blocking layers were formulated at 3.6 and 6.0 weight percent in methanol and Dowanol PM, and at 2 weight percent in t-butanol. Standard drying conditions were used when crosslinking agent was not added. Since no poly(4-vinylpyridine) adhesive layer was coated in these devices, charge generator and charge transport layers were applied as described in Example I. The devices were charge-erase cycled for 200 cycles at ambient RH (12-21 percent) using the indicated cyclic scanners

TABLE O

Device No	$[\eta]$	P(HEMA) Blocking Layer Thickness (µm)	Solvent	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
VIIa	0.272	0.5-0.7	Methanol	310	310	36	86
VIIb	0.272	0.8-1.0	Methanol	370	320	36	50
VIIc[c]	0.654 (X-linked)	0.5-0.7	Methanol	695	640	40	65
VIId	0.654	0.5-0.7	Methanol	540	560	40	104
VIIe[c]	0.654 (X-linked)	0.8-1.0	Methanol	885	885	35	35
VIIf	0.654	0.8-1.0	Methanol	800	920	52	80
VIIg[c]	0.654 (X-linked)	0.5-0.7	DowPM	840	1000	30	75
VIIh	0.654	0.5-0.7	Dow PM	880	1040	90	200
VIIi	0.654	0.8-1.0	Dow PM	830	970	76	85
VIIj	0.654	0.2-0.4[a]	t-Butanol	600	380	40	44
VIIk	0.654	0.2-0.4[b]	t-Butanol	720	500	50	3

a) 2 weight percent solution using a 1.0 mil bar gap

b) 2 weight percent solution using a 1.5 mil bar gap

c) environmental cyclic scanner used; all other devices tested on the ambient cyclic scanner.

The low intrinsic viscosity $[\eta]$ P(HEMA) is clearly inferior to the high viscosity material at both thicknesses. The electrical results obtained for the low molecular weight P(HEMA) blocking layers in this device formed on LE 16610 conductive layers were very similar to those obtained on polypyrrole conductive layers, all other layers being equal (compare devices Va and Vb with VIa and VIIb). The charge depletion (low V_O) mechanism due to interlayer mixing effects discussed in Example V also applies here. In this Example, the evidence for interlayer mixing is more compelling. In devices VIIa and VIIb, the V_O values are less than V_O for the same device without a blocking layer (Example I). This result requires that the generator and/or transport layers have become more dark conductive, and provides strong evidence that an electrically significant quantity of conductive material from the LE16610 conductive layer has migrated and mixed into the upper two layers during coating thereof.

The impact of glutaraldehyde crosslinking is most noticeable in the thinner (0.5-0.7 vs. 0.8-1.0 micrometer) blocking layer devices when high molecular weight P(HEMA) is used as the hole blocking polymer. The crosslinked device VIIc charges 155 volts higher than its sister device (VIId) which has not been crosslinked. The crosslinked P(HEMA) blocking layer is better able to function as a barrier layer and so more effectively blocks upward migration and mixing of LE16610 conductive layer components into the generator and transport layers during coating thereof. In addition, crosslinking the P(HEMA) blocking layer reduces V_R cycle-up because hole trapping P(HEMA) remains fixed in place in the crosslinked blocking layer. Thus, the P(HEMA) cannot be carried upwards by migrating conductive materials because the crosslinked P(HEMA) layer itself significantly decreases the extent of conductive material migration which is the primary cause of trapping and V_R cycle-up. When the high molecular weight P(HEMA) blocking layer thickness is increased to 0.8-1.0 micrometer, electrical effects due to crosslinking (VIIe vs VIIf or VIIi) become indiscernable. The increased P(HEMA) blocking layer thickness alone is sufficient to impart solvent resistance and barrier (to mixing) properties making P(HEMA) crosslinking unnecessary in thicker blocking layers.

Devices which contain uncrosslinked high molecular weight P(HEMA) blocking layers of 0.5-0.7 micrometer thickness (VIId and VIIh) differ significantly in V_R cycle-up. The larger V_R cycle-up for VIIh versus VIId implies that the change in blocking layer coating solvent to the more organic Dowanol PM (from methanol) is at least, in part, responsible for the trapping and V_R cycle-up. Apparently, the propylene glycol methyl ether (Dowanol PM) solvent is more effective than methanol in penetrating and uprooting LE16610 conductive layer components. This solvent induced conductive layer component migration into the blocking layer disrupts and decreases the hydroxyl-hydroxyl hydrogen bonding density in the blocking layer. Consequently more electron trap sites are generated in the lower density hydroxyl-hydroxyl H-bonding areas and this results in the larger V_R cycle-up. Fortunately, in thicker uncrosslinked high molecular weight P(HEMA) blocking layer devices (VIIf and VIIi), the magnitude of this mixing phenomenon (and the resulting V_R cycle-up) is decreased irrespective of which blocking layer coating solvent is used.

Identical devices VIId and VIIh differ markedly in V_O (by 340 volts). Since the only formulation variation in the two devices is the change in blocking layer coating solvents, this change must in part be responsible for the V_O decrease. The lower boiling methanol cast coatings apparently loose their solvent too rapidly so that thin and thick areas arise because of insufficient polymer flow. The thin areas of such a non-uniform blocking layer become prime sites for hole injection from the conductive layer. However, blocking layer thinness is not a sufficient explanation for low V_O since 0.2 micrometer methanol cast P(HEMA) blocking layers are sufficiently thick to block hole injection (Example IV) on carbon impregnated Tedlar® bulk conductive substrates. The combination of a thin blocking layer area superimposed on/or around a conductive layer vertical protrusion (both layers being non-uniform in thickness) provides the most complete physical picture of interfacial sites contributing to V_O decline. Thus, the blocking layer-conductive layer formulation interdependency strongly controls V_O & V_R, except when thicker high molecular weight P(HEMA) blocking layers are used (devices VIIf and VIIi). Then the coating solvent effect on V_O disappears because now even the non-uniform thin areas in the methanol coated blocking layers are sufficiently thick to block hole injection from the LE16610 conductive layer. Thus, the use of thick P(HEMA) coatings as blocking layers eliminates considerably the deleterious impact of non-uniform coating thicknesses on charge-erase electrical properties.

The low charging levels exhibited by t-butanol coated P(HEMA) blocking layers simply indicates the presence of an overall thinner blocking layer which must exist because of the high molecular weight P-(HEMA) solubility limitation (2 weight percent) in t-butanol, as described in Example V. Thus, the significantly thinner t-butanol coated P(HEMA) blocking layer, even if uniform in thickness, is porous to charge injection from the LE16610 conductive layer.

EXAMPLE VIII

This Example illustrates the use of both P(HEMA) and P(HPMA) as vinyl hydroxy ester polymer blocking layers of various thicknesses on strongly injecting binderless cuprous iodide conductive layer. The conductive layers for all the devices in this Example were drawbar coated as described in Example I on Tedlar® substrates. The P(HPMA), available from Polysciences, was coated (0.5 mil drawbar gap) from 3.6 and 6.0 weight percent solutions in 90/10 by weight isobutanol/isopropanol to give the thicknesses in the following table. The moderate viscosity P(HEMA) $[\eta]$ = 0.506 was coated from 6 and 10 weight percent methanol solutions using 0.5 and 5.0 mil drawbar gaps to give 0.8-1.0 and 8.5 micrometer blocking layers, respectively. The very thick P(HEMA) blocking layer was measured directly with the Dektak® stylus whereas the other thicknesses were estimated from the dry thickness - concentration curve developed for P(HPMA) as described in Example II. A nominally thin (0.4-0.6 weight percent ~ 0.06 micrometer) P(4VPy) adhesive layer was drawbar coated (0.5 mil bar gap) and dried as described in previous examples. The charge generator and transport layers were next applied as described in Example I. The devices were cycled using the ambient cyclic scanner for either 1,450 or 12,000 cycles at ambient RH.

TABLE P

Device No.	Blocking Layer Composition	Thickness (micrometers)	X-Cycles	$V_{O(1)}$	$V_{O(X)}$	$V_{R(1)}$	$V_{R(X)}$
VIIIa	P(HPMA)	0.5-0.7	1,450	730	680	35	25
VIIIb	P(HPMA)	0.8-1.0	1,450	680	640	30	24
VIIIc	P(HEMA)	0.8-1.0	12,000	1,200	1,000	20	58
VIIId	P(HEMA)	∽8.5	12,000	1,200	1,400	24	174

Both the P(HPMA) and P(HEMA) blocking layers contribute electrically significant hole blocking capability. The same cuprous iodide conductive layer device, without a blocking layer in Example I, charges to only 90 volts. indicating the blocking layers used in the devices of this Example have significantly inhibited charge injection. The very thick P(HEMA) blocking layer device VIIId has a nominally low V_R at cycling onset and cycles up to only 174 volts in 12,000 cycles. The relatively small V_R cycle-up level observed for the 8.5 micrometer P(HEMA) blocking layer device implies that the natural abundance of electron trapping sites in P(HEMA) is small versus other much thinner blocking layer polymers used in this embodiment, and that the P(HEMA) is less likely to migrate into the CGL and CTL where hole trapping can occur. The lower migration aptitude of P(HEMA) versus other hole blocking layer polymers emerges from P(HEMA) insolubility in commonly used organic coating solvents such as methylene chloride, tetrahydrofuran and toluene. The quantity of electron trapping sites in these vinyl hydroxy ester or vinyl hydroxy amide polymer blocking layers is very likely related to the quantity of disrupted hydrogen bonding density areas (hydrophobic areas) and/or to different levels of dielectric breakdown during xerographic discharge.

Blocking layers containing high molecular weight P(HEMA) ($[\eta]$ = 0.654) were also charge-erase evaluated on strongly injecting CuI conductive layers prepared as previously described in this Example. The P(HEMA) blocking layers were coated using standard 3.6, 6.0 and 2.0 weight percent solutions in Dowanol PM and t-butanol as indicated in the following table. In addition, two devices contained blocking layers which contained glutaraldehyde crosslinked P(HEMA) in which the mole ratio of P(HEMA) repeat units to moles of glutaraldehyde was about 3:1. Since no adhesive layer was applied in these devices, the charge generator and transport layers were next applied as described in Example I.

TABLE Q

Device No.	P(HEMA) Blocking Layer Thickness (micrometers)	Solvent	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
VIIIe^{d}	0.5-0.7	Dow PM	1040	1130	15	28
VIIIf^{d}	0.2-0.4	t-butanol	1020	1020	18	38
VIIIg^{d}	0.2-0.4	t-butanol^{c}	1015	1010	16	22
VIIIh^{a,e}	0.2-0.4	t-butanol^{c}	870	870	25	25
VIIIi^{b,e}	0.8-1.0	Dow PM	920	920	25	25

a) 0.2g P(HEMA), 9.8g tertiary butyl alcohol and 0.21g of 25 weight percent aqueous glutaraldehyde dried at 120°C for one hour.

b) 0.6g P(HEMA), 9.4g Dowanol PM and 0.62g of 25 weight percent aqueous glutaraldehyde dried at 120°C for one hour.

c) A 1 mil bar gap used instead of the usual 0.5 mil bar gap.
d) The ambient cyclic scanner was used.
e) The environmental cyclic scanner was used.

Clearly all of the above devices charged well and retained their charging level in 200 cycles when compared to the 90 volt charging level obtained for the same cuprous iodide device having no blocking layer (Example I). Even the thin, 0.2-0.4 micrometer, high molecular weight P(HEMA) blocking layers prevented electrically deleterious charge injection affording devices with xerographically useful electrical properties. Crosslinking the P(HEMA) blocking layers did not improve cycling properties. The fact that such thin high molecular weight P(HEMA) blocking layers block hole injection on the strongly injecting CuI conductive layers implies that the thin CuI conductive layers have very small vertical protrusions, if any. That CuI conductive layers should have a small thickness variation is reasonable since these conductive layers are very thin (200-1000 Angstroms). The absence of V_R cycle-up in the above devices verifies the incompatibility between inorganic CuI and the organic coating compositions subsequently applied. Thus, CuI conductive layer mixing and migration is electrically insignificant.

EXAMPLE IX

The preparation and blocking layer use of three different copolymer compositions derived from HEMA and 4-VPy are illustrated in this Example. The three copolymers were prepared according to the following general procedure.

Both monomers were individually first passed three times through a De-Hibit 100 column, as described in Example IV, to remove hydroquinone based polymerization inhibitors. The pure monomers, the tertiary butyl alcohol solvent and the AIBN polymerization (0.3 mole percent based on total monomers charged) initiator were charged to the same reaction vessel and accessories described in Example IV. The polymerization solution was magnetically stirred and argon gas was passed through the solution throughout the polymerization. Finally the resulting polymer was coagulated, filtered, washed, and dried as described in Example IV. The following table defines the polymerization charges, conditions and compositional results for the three copolymers prepared.

TABLE R

Copolymer No. (grams solvent)	Monomers Charged				Polymerization Conditions		Yield	Polymer Composition Mole % Repeat Unit	
	HEMA		4VPy		Time (hrs)	Temp. (°C)	Grams (%)	P(HEMA)	P(4VPy)
	grams	moles (mole%)	grams	moles (mole%)					
IXa (150)	21.84	1.678×10^{-1} (84)	3.38	3.22×10^{-2} (16)	15	66	17.93 (71)	91	9
IXb (150)	17.65	1.356×10^{-1} (68)	6.77	6.44×10^{-2} (32)	15	57	12.20 (50)	64	36
IXc (150)	13.01	1.00×10^{-1} (50)	10.51	1.00×10^{-1} (50)	16	62	10.50 (45)	40	60

The final copolymer composition was determined from the ^{1}H-NMR spectrum obtained at ambient temperature on a Bruker WP-80 instrument from a DMSO-d_6 polymer solution at 5 weight percent. The integrated normalized pyridine ring hydrogen signals were compared to the integrated P(HEMA) hydroxyl hydrogen signal to give the compositional values in the table immediately above. All three copolymers, at a concentration of 1 weight percent, failed to dissolve in toluene, tetrahydrofuran, and methylene chloride indicating these copolymers, like P(HEMA) itself, also form a bulk solvent barrier towards the subsequently used coating solvents required to complete fabrication of the device.

The incentive for using copolymers derived from the hole blocking P(HEMA) repeat units and the P-(4VPy) adhesive repeat units was to combine in one coated layer both properties (blocking and adhesive), thus eliminating the need to coat a separate adhesive layer in these devices on non-metallic conductive layers. Consequently, no separate P(4VPy) adhesive layer was coated. The bulk conductive substrate, carbon impregnated Tedlar® (CIT), was used as the conductive layer. The three copolymers were coated (drawbar gap 0.5 mil) from 6 weight percent t-butanol solutions to give blocking layers of 0.8-1.0 micrometer thickness after drying at standard conditions. In addition, the 64:36 composition copolymer was coated from 2.0 and 3.6 weight percent t-butanol solutions to give 0.2-0.4 and 0.5-0.7 micrometer blocking layers. The blocking layer thicknesses were estimated from the previously described (Example II) dry thickness-concentration curve developed for P(HPMA). Charge generator and transport layers were next applied as described in Example I, and the charge-erase cycling data were obtained at ambient RH using the ambient scanner.

TABLE S

Device No.	Blocking Layer Composition P(HEMA-4VPy) Copolymer Mole % R.U.	Blocking Layer Thickness (micrometer)	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
IXd	91-9	0.8-1.0	880	920	40	60
IXe	64-36	0.2-0.4	960	1000	50	50
IXf	64-36	0.5-0.7	860	1000	50	80
IXg	64-36	0.8-1.0	980	1000	50	75
IXh	40-60	0.8-1.0	880	900	50	90

Examination of the 0.8 micrometer blocking layer data in the above table indicates a steady increase (60 to 75 to 90 volts) in $V_{R(200)}$ with increasing P(4-VPy) repeat unit content in the copolymer. It is very likely that the basic nitrogens in the P(4-VPy) repeat units of the copolymer disrupt the dense intermolecular hydroxyl-hydroxyl hydrogen bonding normally found in the P(HEMA) homopolymer. This dense hydroxyl-hydroxyl H-bonding interaction structurally resembles H-bonded water and presumably assists, along with a small amount of H-bonded water, in the transport of photodischarged electrons through the relatively thick blocking layers. However, when the hydroxyl-hydroxyl H-bonding density is disrupted by larger amounts P-(4-VPy) repeat units in the copolymer, other hydrogen bonding structures result that are not as capable as the hydroxyl-hydroxyl H-bonded structure in transporting the photodischarged electrons through the entire thickness of the blocking layer. Consequently more photodischarged electron trap sites are created which trap the electrons and the trapping appears as V_R cycle-up.

An alternative or simultaneous mechanism for increased V_R cycle up with increased P(4-VPy) content in the copolymer invokes blocking layer copolymer migration into the generator layer during coating of the CGL and/or CTL. Migration would be expected to increase with increasing P(4-VPy) content in the copolymer because the homopolymer P(4VPy) is soluble in the CGL coating solvent, methylene chloride. Thus, the copolymer richest in P(4-VPy) content, the 40:60 copolymer, would be most likely to migrate into the CGL and CTL while coating the latter. Although the three copolymers failed to dissolve at the one weight percent level in methylene chloride, some low finite copolymer concentration does dissolve and migrate. Very low polymer solubilities and migration levels (ppm) are sufficient to cause electrically noticeable hole trapping in the generator layer as V_R cycle-up. Further inspection of the above table indicates that even the thinnest 0.2-0.4 micrometer blocking layer provides good blocking of hole injection on the solvent resistant CIT conductive layers (versus the same device in Example I without a blocking layer). Similar results were found for devices containing 100 percent P(HEMA) blocking layers on CIT (Example IV) at both ambient and low RH.

The second electrical data set of this Example describes charge-erase cycling of devices containing three blocking layer thicknesses of the 64:36 copolymer on CIT conductive layers. Three concentrations of the 64:36 copolymer in t-butanol (1.8, 3.6 and 14.4 weight percent) were drawbar coated (0.5 mil gap) to give estimated blocking layer thickness ranges of 0.2-0.4, 0.5-0.7 and 2.0-2.4 micrometers. Since no P-

(4VPy) adhesive layer was coated, charge generator and transport layers were applied as described in Example I. The completed devices were charge-erase cycled with the ambient scanner at both ambient and low RH.

Device No.	64:36 Copolymer Blocking Layer	%RH	$V_{(X\ Cycles)}$	$V_{O(1)}$	$V_{O(1200)}$	$V_{O(X)}$	$V_{R(1)}$	$V_{R(1200)}$	$V_{R(X)}$
IXi	0.2-0.4	24	4415	890	970	920	30	37	40
IXi	0.2-0.4	<5	2260	860	1040	1040	35	90	80
IXj	0.5-0.7	24	4415	780	910	810	28	55	60
IXj	0.5-0.7	<5	2260	780	1050	1040	38	170	145
IXk	2.0-2.4	24	4415	840	1040	1100	35	85	165
IXk	2.0-2.4	<5	2260	850	1200	1230	65	250	260

As in the first data set of this Example, V_R cycle-up increased with blocking layer thickness but the magnitude of the cycle-up is exacerbated at low RH (<5%). In 2,260 charge-erase cycles, only the thin 0.2-0.4 micrometer blocking layer device exhibits a moderate V_R cycle-up. In the thicker blocking layer devices, more trap sites are available for electron trapping so initial V_R and V_R cycle-up are larger. The electron trap sites in this copolymer blocking layer are presumably created at low RH when some of the small amount of trapped water (which assists electron transport) escapes leaving hydrophobic lower hydrogen bonding density areas, through which photodischarged electrons cannot pass or become trapped. The remaining hydroxyl-hydroxyl H-bonding, that is not disrupted by pyridine-hydroxyl hydrogen bonding in these copolymers, is of insufficient density to compensate for the decreased water content at low RH. The net result is electron trapping and V_R cycle-up. The adhesion of the P(HEMA-4VPy) copolymer blocking layers to the t-Se/PVK generator layers in this Example was comparable to that obtained with a separate P(4VPy) adhesive layer applied on top of a high molecular weight P(HEMA) blocking layer. Thus, similar adhesion was attainable without fabricating a separate P(4VPy) adhesive layer. The P(4VPy) repeat units in the P-(HEMA-4VPy) blocking layer provide interfacial adhesion to the t-Se/PVK generator layer via a similar mechanism as does the separately coated P(4VPy) adhesive layer while still providing useful cyclic electrical properties, provided that the blocking layer is not too thick.

EXAMPLE X

This Example illustrates the preparation of four additional P(HEMA) copolymers containing repeat units of poly(2-hydroxypropylmethacrylate) [P(HPMA)] and poly(N-vinylpyrrolidone) [P(VP)] along with the charge-erase blocking layer evaluation of two of the copolymer compositions on carbon impregnated Tedlar® (CIT). The blocking layer copolymers were formulated in Dowanol PM at concentrations of 3.6 and 6.0 weight percent to give approximate thicknesses of 0.5-0.7 and 0.8-1.0 micrometer based on the P-(HPMA) dry thickness-concentration curve in Example II. Blocking layers were drawbar coated (0.5 mil gap) and then dried at standard conditions. As in Example IX, the incentive for using these P(HEMA) copolymers as blocking layers was to improve adhesion to the PVK based generator layer, so no separate P(4VPy) adhesive layer was applied. The charge generator and transport layers were formulated, coated and dried as described in Example I.

The four copolymers were prepared according to the following procedure. The HEMA (Mhoromer BM-920) and HPMA (Mhoromer BM-955) monomers were first passed three times through a De-Hibit 100 column, as described in Example IV, to remove the hydroquinone based polymerization inhibitors. The N-vinylpyrrolidone (98 percent from Aldrich Chem.) monomer (~16 grams) was dissolved in 250 ml toluene and 15 ml of deionized water was added. The two liquid layers were shaken in a separatory funnel thus transferring the 0.1 percent KOH polymerization inhibitor from the monomer-toluene phase to the aqueous phase. This extraction was repeated a second time and the toluene layer was separated and rotoevaporated under reduced pressure at 50° C to yield monomer suitable for copolymerization.

Copolymers derived from monomer combinations of HEMA-HPMA, HEMA-VP and HPMA-VP were previously prepared in bulk polymerizations frequently containing low added levels of difunctional vinyl monomer for crosslinking, with and without polymerization initiators, at 60-70 °C in 12 hours. This work is described in U.S. 3,721,657 with the resulting polymer hydrogels being suitable for contact lens and membrane applications. This procedure was modified using tertiary butyl alcohol as a polymerization solvent and AIBN (at 0.3 mole percent based on total monomer weight charge) as the polymerization initiator without an added crosslinking agent. Alcohol soluble vinyl hydroxy ester based polymeric materials were sought for solvent coating the blocking layer. Crosslinking agents may be added to the already formed polymer in the coating solution used to coat the blocking layer composition. Crosslinking then occurs in a convection air oven at 100 - 120 °C while the solvent was removed from the blocking layer coating. Crosslinking of P(HEMA) or P(HPMA) repeat units in copolymer blocking layer applications may be achieved through formation of acetal groups, when using a dialdehyde (such as glutaraldehyde).

To a 1 liter 3 neck round bottom flask, equipped as described in Example IV, was charged the pure HEMA monomer and the comonomer (M2 is HPMA or VP) and the AIBN polymerization initiator. The polymerization solution was magnetically stirred with argon passed through the solution throughout the polymerization. After cooling the reaction vessel contents, the polymer solution or dispersion, was coagulated into toluene (9.0 - 9.5 x the volume of polymer solution) and the precipitated polymer was filtered on a coarse glass frit using vacuum. The solvent moist copolymer was next dried at 50-70 °C overnight in a vacuum oven at <0.5 mm Hg. The following in TABLE U defines the polymerization charges, conditions and compositional results for the four copolymers prepared.

TABLE U

Copolymer	Monomers Charged				Polymerization Conditions		Yield	Polymer Composition	
No	HEMA		M2		Time	Temp	Grams	Mole % Repeat Unit	
(grams solvent)	grams	moles (mole%)	grams	moles (mole%)	(hrs)	(°C)	(%)	HEMA	M2
			HPMA						
Xa	40 00	$3\,073\times10^{-1}$	44.30	$3\,073\times10$	19.5	78	66 07	59	41
(480)		(50)		(50)			(78)		
			HPMA						
Xb	60 00	$4\,610\times10^{-1}$	22 16	$1\,537\times10^{-1}$	19 5	76	66 50	81	19
(480)		(75)		(25)			(81)		
			VP						
Xc	40 00	$3\,073\times10^{-1}$	16.07	$1\,446\times10^{-1}$	17.5	83	51 40	80	20
(340)		(68)		(32)			(92)		
			VP						
Xd	50.00	$3\,840\times10^{-1}$	10.68	$9\,600\times10^{-2}$	17 5	79	54 15	88	12
(360)		(80)		(20)			(89)		

The final copolymer compositions were determined from ^{13}C-NMR obtained on a 100 MHz Bruker WH400 instrument from a 5 weight percent DMSO-d_6 solution. The integrated peak areas for the methylene group attached to the carboxyl in P(HEMA) and P(HPMA) repeat units (at 66 and 69.5 ppm respectively versus the center line of DMSO at 39.5 ppm) were compared to the integrated peak area for the methylene group attached to the carbonyl in vinylpyrrolidone at 31 ppm to give the copolymer compositions in the above table. All four copolymers were practically insoluble in methylene chloride at room temperature (< 0.02 weight percent solubility at a 0.1 weight percent initial concentration) and in toluene (< 0.1 weight percent solubility) as well. In tetrahydrofuran, three of the four copolymers were insoluble but the 59:41 P(HEMA - HPMA) copolymer did dissolve at 0.1 weight percent consistent with the moderate solubility of poly(2-hydroxypropylmethacrylate) in tetrahydrofuran. Thus, these copolymer blocking layers will also co-function as a solvent barrier layer towards methylene chloride, toluene and, for the most part, tetrahydrofuran.

The charge-erase cyclic electrical properties for two P(HEMA) copolymers at ambient RH (18 percent) are provided in TABLE V below using the ambient cyclic scanner and CIT as the conductive layer.

TABLE V

Device No.	Blocking Layer		$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
	Composition P(HEMA-M2) Copolymer Mole % R.U.	Thickness (µm)				
Xe	P(HEMA-HPMA) 59-41	0.5-0.7	840	770	27	40
Xf	P(HEMA-VP) 88-12	0.8-1.0	840	850	24	35

Electrical evaluation of both copolymer compositions show that hole injection is adequately blocked (high V_O versus the same device without a blocking layer in Example I) and photodischarge electron trapping in the 0.5-1.0 micrometer thick blocking layer range is minimal. Similarly, photodischarge hole trapping in the generator layer, usually found when some of the blocking layer polymer has migrated into the generator layer, is minimal based on the small V_R cycle-up. These copolymers provide adequate charge-erase electrical properties at ambient RH along with sufficient interfacial adhesion to maintain device integrity during routine handling.

EXAMPLE XI

This Example illustrates the preparation and use of hole blocking layers comprised of homogeneous polymeric complexes derived from P(HEMA) ($[\eta]$ = 0.654) and poly(ethyloxazoline) combined in various repeat unit molar ratios. The poly(ethloxyazoline) used was P(EOx) 500, having a Mw of 500,000 from Dow Chemical. Two conductive layers were used: ICP-117 polypyrrole and carbon impregnated Tedlar (CIT). The ICP-117 conductive layers were drawbar coated from the Polaroid provided dispersions, diluted to 5 weight percent, onto Tedlar® (1.5 mil gap) and Mylar (0.5 mil gap). After drying the ICP-1 17 conductive layers as described in Example I, the blocking layer formulations were drawbar coated (0.5 mil bar gap) from approximately 6.0 and 3.6 weight percent methanol solutions to give dry thicknesses of 0.8-1.0 and 0.5-0.7 micrometer. The thicknesses were estimated from the Dektak® generated curve for P(HPMA) in Example II. After combining the two blocking layer polymers in the appropriate quantities, methanol was added and the mixture was warmed gently (40-50° C.) to give the desired solids level solution. Standard blocking layer drying conditions (Example II) were applied and then the charge generator and transport layers were applied as described in Example I. Since the incentive for using these P(EOx)-P(HEMA) hydrogen bonding complexes as blocking layers was to improve adhesion to the PVK generator layers, the P(4VPy) adhesive layer was omitted.

The homogeneous hydrogen bonding polymer complexes, used as blocking layer compositions, are described in the following table.

TABLE W

Blocking Layer Compositions

Device No.	Repeat Unit Mole Percent P(EOx)-P(HEMA)	Weight Percent P(EOx)-P(HEMA)	Weight Percent Polymers in Methanol
XIa	54-46	47-53	6.0
XIb	43-57	36-64	5.8
XIc	30-70	25-75	5.7
XId	16-84	13-87	6.0
XIe	8.5-91.5	7-93	6.0
XIf	7-93	5.5-94.5	3.6

PEOx is known to compatibilize normally incompatible hydroxylic polymers such as the Bakelite Phenoxy resins (Keskkula, H., and Paul, D.R. Proc. Div. PMSE ACS Meeting, St. Louis, MO. 50, 11 (1984) and polyvinylphenol (P. Lin, T.K. Kwei, E.M. Pearce, K. Clash-Paper 106, Polymer Chemistry Div. 192nd National ACS Meeting, Anaheim, CA, Sept. 1986). Homogeneous polymer blends were obtained with the P-(EOx) and P(HEMA) combined in repeat unit molar ratios from 54-46 to 7-93. Scanning electron micrographs (640 to 10,000x) of 0.8-1.0 micrometer coatings of these blends indicated no phase separation whatsoever. The ambient cyclic scanner was used to generate charge-erase cyclic data at both ambient and low RH for the indicated number of cycles.

TABLE X

Device No.	Blocking Layer Composition P(EOx) - P(HEMA) Repeat Unit Mole %	%RH	$V_{(X\ cycles)}$	$V_{O(1)}$	$V_{O(200)}$
$XIa^{a,c}$	54-46	24	200	1020	1150
$XIb^{a,c}$	43-57	24	200	1040	1150
$XIc^{a,c}$	30-70	24	200	970	1050
$XId^{a,c}$	16-84	24	3015	860	1030
$XId^{a,c}$	16-84	<5	3515	1000	1250
$XIe^{b,c}$	8.5-91.5	20	2250	760	790
$XIe^{b,c}$	8.5-91.5	<5	3560	760	---
$XIf^{b,d}$	7-93	20	2250	550	---
$XIf^{b,d}$	7-93	<5	3560	520	---
$XIa^{a,c}$	---	70	200		---
$XIb^{a,c}$	---	60	140		---
$XIc^{a,c}$	---	55	95		---
$XId^{a,c}$	980	30	50		45
$XId^{a,c}$	1100	60	235		168
$XIe^{b,c}$	760	50	50		65
$XIe^{b,c}$	800	60	---		60
$XIf^{b,d}$	740	250	---		350
$XIf^{b,d}$	590	240	---		270

a) On conductive substrate: Carbon impregnated Tedlar®.

b) On conductive layer: ICP-117 polypyrrole-polymer complex.

c) Estimated blocking layer thickness: 0.8-1.0 micrometer.

d) Estimated blocking layer thickness: 0.5-0.70 micrometer.

Inspection of the electrical data in the abcve TABLE X indicates several trends as a function of H-bonded polymeric complex composition, RH testing conditions and blocking layer thickness. At a blocking layer thickness of 0.8-1.0 micrometer and at ambient (20-24%) RH, devices XIa - XIe show a well defined trend in V_R cycle-up. As the P(EOx) content decreases, the V_R cycle-up also decreases. This implies that some hole trapping P(EOx), when present as a blocking layer component in larger quantities, is not sufficiently anchored (by means of H-bonding) in the blocking layer and migrates into the generator and/or transport layer during coating of these layers. The migrated P(EOx) then traps holes in these layers which, as an ongoing process with charge-erase cycling, appears as V_R cycle-up. Since P(EOx) is soluble in tetrahydrofuran and methylene chloride, two of the three subsequently used coating solvents, P(EOx) migration during coating of the generator and transport layers is a likely occurrence. When the P(EOx) content is further reduced to <10 mole percent of the polymeric repeat units present in an 0.8-1.0 micrometer thick blocking layer (device XIe), very little P(EOx) migration occurs as evidenced by the small V_R cycle-up, even at low RH. In contrast, device XId, which has 16 mole percent P(EOx), has high residual voltages at low RH, but not at ambient RH. This result implies that when the P(EOx) content is sufficiently large, a second charge trapping mechanism dependent on water content is operative. Increasing P(EOx) content disrupts the dense hydroxyl-hydroxyl hydrogen bonding level [present in 100% P(HEMA) blocking layers] which is believed to assist photodischarged electron transport through the blocking layer. In addition, since the devices are first humidity conditioned at <5% RH for 16-24 hours prior to charge-erase cycling at <5% RH, some loss of the small amount of H-bonded water in the blocking layer occurs. When present in vinyl hydroxy ester or vinyl hydroxy amide polymer blocking layers, the H-bonded water functions as a hydroxyl-hydroxyl bridging vehicle which extends the intermolecular hydrogen bonding sequence lengths between repeat units in adjacent polymers. The extension of hydroxyl-hydroxyl hydrogen bonding particularly occurs in vinyl hydroxy ester or vinyl hydroxy amide polymer blocking layer areas that are naturally lacking this hydrogen bonding mode because the low molecular weight water molecule is solid state mobile and seeks to maximize its hydrogen bonding environment without disrupting already existing stable hydrogen bonding areas. Thus, when the H-bonded water level is reduced in vinyl hydroxy ester or vinyl hydroxy amide polymer blocking layers at low RH, hydrophobic gaps form and trap photodischarged electrons leading to higher V_R and V_R cycle-up. So the combination of decreased water content and increased P(EOx) copolymer content distorts optimum electron transport conditions. It may also be possible that P(EOx), which has migrated into the CGL and/or CTL during coating thereof, after dehydration becomes a more efficient hole trapping source than the hydrated P(EOx), so V_R cycles up more rapidly at low RH.

The initial charging levels for devices XIe and XIf on the ICP-117 polypyrrole conductive layer indicate this conductive layer to be more hole injecting versus carbon impregnated Tedlar®, which is used in all the other devices. Inspection of the V_O levels for the same devices containing no blocking layer in Example I verifies the above hole injection capability. Furthermore, decreasing blocking layer thickness (XIf vs. XIe) decreases V_O implying insufficient blocking layer thickness over the high areas of the ICP-117 conductive layer. A second mechanism contributing to V_O decline which cannot be precluded with the ICP-1 17 devices involves migration and mixing of conductive layer components into the CGL and/or CTL during coating thereof. The CIT conductive layer devices (XIa-XId) are more uniform and more resistant to coating solvent effects so V_O levels are higher and remain higher with cycling. The P(EOx)-P(HEMA) hydrogen bonding polymeric complexes used as blocking layer materials in this Example provide sufficient interfacial adhesion to maintain device integrity during routine handling procedures.

EXAMPLE XII

This Example illustrates the use of 0.8-1.0 micrometer thick blocking layers of P(HEMA) copolymers and the P(HEMA)-P(EOx) hydrogen bonded polymeric complex. The blocking layers were drawbar coated (0.5 mil gap) onto strongly injecting spray coated cuprous iodide ground planes wherein the cuprous iodide coatings were spray fabricated as described in Example I. Mylar polyester (E.I. duPont de Nemours & Co.) substrates were used for all devices. The 6 weight percent blocking layer coating solutions consisted of 0.6 gram polymer(s) in 9.4 grams of methanol or Dowanol PM solvent. Methanol was used for the P(HEMA-4VPy) copolymer and the P(HEMA)-P(EOx) complex, and Dowanol PM was used as solvent for the other three P(HEMA) copolymer blocking layer solutions. Blocking layer thickness was estimated from the dry thickness-concentration calibration curve and standard drying conditions were used for all coated layers as in Examples I and II. No adhesive layer was necessary at the blocking layer-generator layer interface since device integrity was maintained during routine handling and electrical evaluation. The charge generator and transport layers were applied as described in Example I, and the ambient cyclic scanner was employed to obtain charge-erase cycling data at ambient RH. The following charge-erase data in TABLE Y were obtained.

TABLE Y

Device No.	Blocking Layer Composition Mole % Repeat Units	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
XIIa	P(HEMA-HPMA) Copolymer 81-19	770	880	10	16
XIIb	P(HEMA-HPMA) Copolymer 59-41	840	850	15	36
XIIc	P(HEMA-VP) Copolymer 88-12	770	940	27	32
XIId	P(HEMA-4VPy) Copolymer 64-36	860	960	31	70
XIIe	P(HEMA)-P(EOx) Complex 93-7	910	930	26	50

The preparation and analyses of the above blocking layer compositions were provided in Example X (for XIIa, XIIb and XIIc), Example IX (for XIId) and Example XI (for XIIe). Inspection of the above TABLE Y indicates satisfactory hole blocking for all the devices when V_O is compared to the same device without a blocking layer (V_O of 90 volts) in Example I. It is interesting to note that a $V_{R(200)}$ of 70 volts for device XIId is very similar to the $V_{R(200)}$ value (75 volts) found for the same (thickness) blocking layer copolymer on (CIT) carbon impregnated Tedlar® (device IXg in Example IX) also at ambient RH charge-erase testing conditions. This implies that V_R cycle-up is independent of conductive layer composition when solvent resistant conductive layers such as CIT and CuI are utilized.

EXAMPLE XIII

This Example illustrates the use of blocking layers derived from the 64:36 (repeat unit molar ratio) HEMA-4VPy copolymer, and various blend compositions (H-bonded polymeric complexes) of P(HEMA) and P(EOx) on conductive carbon black layers of olefinic flash primer LE16610 (Red Spot Paint & Varnish Co.). The conductive layers were formulated, sprayed and dried on Mylar substrates as described in Example I. All blocking layer compositions were coated from methanol solution at 3.6 and 6.0 weight percent to give 0.5-0.7 and 0.8-1.0 micrometer thicknesses, respectively. The blocking layer thicknesses were estimated based on a previously described (Example II) dry thickness-coating concentration curve and standard drying conditions were employed. An adhesive layer at the blocking layer-generator layer interface was not needed since the devices maintained their integrity during routine handling and electrical testing. Charge generator and transport layers were applied as described in Example I. Both ambient and low RH charge-erase testing conditions were used to evaluate these devices using the ambient cyclic scanner. The electrical results for the devices containing the 64:36 P(HEMA-4VPy) copolymer blocking layer are indicated in the following table.

TABLE Z

Device No.	P(HEMA-4VPy) Copolymer Blocking Layer - (micrometers)	%RH	$V_{(X cycles)}$	$V_{O(1)}$	$V_{O(X)}$	$V_{R(1)}$	$V_{R(X)}$
XIIIa	0.5-0.7	12	200	460	380	43	76
XIIIb	0.8-1.0	12	200	730	780	46	76
XIIIb	0.8-1.0	<5	1420	700	680	53	110

The charge-erase results for the thin P(HEMA-4VPy) copolymer blocking layer (device XIIIa) indicates that hole injection (low V_O value) is in fact more severe than it is in the same device without a blocking layer (Example I). This implies mixing of hole conductive components from the conductive layer into the generator and/or transport layers during coating of these layers. However, increasing the blocking layer thickness to 0.8-1.0 micrometer provides a blocking layer sufficiently thick to reduce the amount of mixing of the conductive layer components with the upper two layers. Consequently, $V_{O(1 \& 200)}$ increases to levels greater than that found for the same device without a blocking layer. The solvent barrier properties of the 64:36 P(HEMA-4VPy) copolymer blocking layer to subsequently used coating compositions are only sufficient when the blocking layer is at least 0.8-1.0 micrometer.

The V_R cycling behavior for 200 cycles at ambient RH (device XIIIb) is very similar to device XIId (Example XII) and device IXg (Example IX) indicating the conductive layer composition has no significant electrical effect on V_R cycle-up provided that the 64:36 HEMA-P(4VPy) copolymer blocking layer is sufficiently thick on the LE16610 conductive layer.

The ambient V_R cycle-up, as described in Example IX for blocking layers of the same composition, implies blocking layer copolymer migration into the generator and/or transport layers during coating of these layers. Hole trapping then occurs in these layers with the observed associated electrical effect of V_R cycle-up. The more severe V_R cycle-up at low RH implies the simultaneous presence of a second trapping mechanism, which is the same blocking layer electron trapping mechanism described in Example IX.

The P(HEMA)-P(EOx) polymer blend blocking layers were formulated, drawbar coated and dried as described in Example XI. Since all the blocking layers were coated from 6 weight percent methanol solutions, the thicknesses were estimated at 0.8-1.0 micrometer based on the aforementioned calibration curve (Example II). The charge-erase electrical results were obtained with the ambient cyclic scanner at ambient and low RH and are indicated in the following table.

TABLE AA

Device No.	P(EOx)-P(HEMA) Blend Blocking Layer P(EOx)-P(HEMA)[a]	%RH	$V_{O(1)}$	$V_{O(200)}$	$V_{R(1)}$	$V_{R(200)}$
XIIIc	54-46	19	980	1350	90	500
XIIId	43-57	19	1000	1050	40	110
XIIIe	30-70	19	1000	1130	35	35
XIIIe	30-70	<5	880	1100	45	125
XIIIf	16-84	19	900	920	25	25
XIIIf	16-84	<5	780	860	35	50
XIIIf	16-84	<5	860	920[b]	45	112[b]
XIIIf	16-84	24	820	900[c]	35	80[c]

a) Repeat unit molar ratio charged in the polymer blend.

b) After 3515 charge-erase cycles.

c) After 3015 charge-erase cycles.

Since all of the above devices have sufficiently thick 0.8-1.0 micrometer blocking (barrier) layers on this LE16610 carbon black conductive layer, the $V_{O(1\ \&\ 200)}$ values reflect satisfactory hole blocking and little or no conductive layer mixing with subsequently coated layers. However, a V_R cycle-up trend with increasing P(EOx) content in the blocking layer parallels that observed in Example XI, on CIT conductive substrates, for similar reasons. Device XIIIf was charge-erase cycled in the tabulated sequence of the above table wherein V_R cycle-up in each cycling sequence was for the most part recoverable at the beginning of the next cycling sequence. The time between each cycle sequence was 2-3 days as a matter of convenience, but the actual V_R recovery time may be considerably less.

EXAMPLE XIV

This example illustrates the use of high molecular weight P(HEMA) (η = 0.654) as a hole injection blocking layer on titanium coated Mylar (combination of conductive layer and substrate). A P(HEMA) blocking layer, a Se particles dispersed in poly (vinylbutyral) [PVB] CGL, and an N,N'-bis-(3"-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine in polycarbonate (Merlon 50, available from Mobay Chemical Co.) CTL were all sprayed on top of the conductive titanium coated substrate. No adhesive layers were employed at the blocking layer - CGL interface. The spray fabrication of each layer will first be described starting with the P(HEMA) blocking layer.

A 2 weight percent P(HEMA) blocking layer solution was prepared by dissolving 12 grams of P(HEMA) in 588 grams of propylene glycol methyl ether (Dowanol PM, available from Dow Chemical Co.) solvent at room temperature. This solution was sprayed using commercially available spray guns and equipment manufactured by Binks Manufacturing Company. A Model 77 electrostatic spray gun was used in the non-electrostatic mode with a horizontal recipricator. The Model 77 gun was equipped with a N63A fluid nozzle and a N63PC air atomization nozzle. The fluid pressure was 2.2 psi and the spray atomization pressure was 30 psi. With the atomization pressure at 30 psi and the fan angle at 0°, the fan angle air supply was opened until a reading of 170 cu. ft. per hour was obtained on the air flow meter in the atomization line. The spray gun was operated automatically and was traversed (3.8 ft./min.) on the reciprocator while spraying from right to left onto the horizontally postioned mandrel. The conductive substrate (titanium coated Mylar from E.I. duPont de Nemours & Co.) sheets to be sprayed were tape mounted onto the cyclindrical aluminum mandrel which was rotated at a speed of 120 rpm. The P(HEMA) blocking layer was sprayed in one pass and the solvent moist coating was rotated for 3 or 4 minutes after completing the spray process in order to flash off the bulk of the solvent. The partially dried coating was dismounted from the mandrel and dried at 110°C for 20 minutes in an air convection oven. The dry thickness of this P(HEMA) blocking layer was approximately 0.8-1.0 micrometer determined from the weight applied to a known area.

The generator layer (CGL) dispersion was prepared by roll milling trigonal selenium (13.6grams), poly (vinylbutyral) [B-76, available from Monsanto] (3.5 grams) and the solvent mixture comprising 72.2 grams toluene and 24.2 grams tetrahydrofuran for several days (2-5 days). This concentrated dispersion (15 weight percent solids) contained approximately 45 volume percent trigonal selenium and 55 volume percent poly (vinylbutyral). Prior to spraying , the concentrated dispersion was diluted with a 1:1 (by weight) mixture of toluene and THF (141.8 grams each) which was manually swirled for 1-2 minutes to give a sprayable 4.3 weight percent total solids dispersion.

The above dispersion was sprayed using commercially available spray guns and equipment manufactured by Binks Manufactruring Company. A Model 21 non-electrostatic spray gun was used with a horizontal recipricator. The Model 21 gun was equipped with a 63A fluid nozzle and a 63PE air atomization nozzle. The fluid pressure was 5 psi with the needle valve in the fluid nozzle set at 0.75 turns from the closed position. The spray atomization pressure was set as follows. With the fan angle closed to 0° and the air supply at 270 cu. ft./ hour, the fan angle air supply was opened until a reading of 310 cu. ft / hour was obtained on the air flow meter in the atomization line. The spray gun was operated automically and was traversed (3.7 ft./min.) on the recipricator while spraying from right to left on the horizontally placed mandrel. The partial device sheets, consisting of Mylar substrate, titanium conductive layer and P(HEMA) blocking layer, were tape mounted onto the cyclindrical aluminum mandrel which was rotated at a speed of 150 rpm during the spraying application. This selenium-PVB generator layer was sprayed in one pass and the partial device containing the solvent moist generator layer was dismounted from the mandrel and dried at 135°C for 20 minutes in an air convection oven. The dry thickness of this selenium-PVB generator layer was approximately 0.26 micrometer determined from the weight applied to a known area.

The transport layer (CTL) solution was formulated at 5 weight percent solids as follows. Polycarbonate (Merlon M-50) (36 grams) was roll milled with 1140 grams of a solvent mixture comprising 684 grams methylene chloride and 456 grams 1,1,2- trichloroethane for 2-3 days until a solution formed. To this solution was added 24 grams of N,N'-bis-(3"-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine and the mixture was further roll milled overnight to give a sprayable 5 weight percent solution comprising 40 weight percent N,N'-bis-(3"-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine and 60 weight percent Merlon M-50 solids content.

The above CTL solution was spray fabricated onto the dried CGL again using the spray guns and associated equipment available from Binks. A Model 77 spray gun was again used in the non-electrostatic mode in the same Binks spray booth using the same horizontal recipricator. The Model 77 spray gun was equipped with a 0.035 fluid nozzle and a N65PB air atomization nozzle. The fluid pressure was 8.4 psi and the spray atomization pressure was 60 psi. With the atomization pressure at 60 psi and the fan angle at 0°, the fan angle air supply was opened until a reading of 190 cu. ft./ hour was obtained on the air flow meter in the air atomization line. The spray gun was operated automically in a continuous mode and was traversed (3.9 ft./min.) on the recipricator while spraying four passes (right to left and then left to right - 2 ×) onto the horizontally placed mandrel. The partially completed device sheets to be sprayed were tape mounted onto the cyclindrically placed mandrel which was rotated at a speed of 100 rpm. After completion of the four pass CTL spray application, the solvent moist CTL coating was spun for an additional 3-4 minutes to flash off most of the solvent such that the thick CTL coating did not gravity sag when the mandrel was stopped from spinning. The partially dried coating was dismounted from the mandrel and was dried in an air convection oven by slowly increasing the temperature of the oven from 40 to 135°C in 35 minutes followed by isothermal heating at 135°C for 10 minutes. The dry thickness of the CTL was 23.2 micrometers determined from the weight applied to a known area.

The spray fabricated completed devices were charge-erased cycled using the environmental cyclic scanner at ambient RH (35%), low RH (5%), and at high RH (70%). The charge-erase cyclic data for two of these devices at various RH testing conditions is described below.

TABLE BB

Device No.	%RH	X Cycles	$V_O(1)$	$V_O(X)$	$V_R(1)$	$V_R(X)$
XIVa	35	1200	881	895	7	3
	5	200	960	950	10	9
	70	3200	876	950	5	30
	<5	3000	920	870	15	15
XIVb	35	3400	909	942	5	3

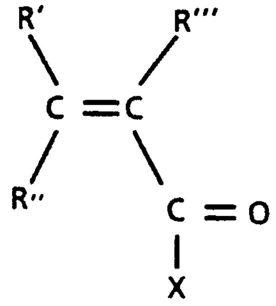
Device XIVa was charge-erase tested under the indicated relative humidity sequence allowing considerable (> 16 hours) equilibration time at the next RH condition prior to charge-erase testing at that new RH condition. Device XIVa maintained its high charging level and low residual voltage (V_R) at all relative humidities used in this test. These results indicate that hole injection from the titanium conductive layer has been substantially blocked by the P(HEMA) blocking layer and that charge trapping remains low (low V_R) with repeated xerographic cycling.

Although the invention has been described with reference to specific preferred embodiments, it is not intended to be limited thereto, rather those skilled in the art will recognize that variations and modifications may be made therein which are within the spirit of the invention and within the scope of the claims.

Claims

1. An electrophotographic imaging member comprising a supporting substrate having an electrically conductive surface, a charge blocking layer comprising a vinyl hydroxy ester or vinyl hydroxy amide polymer, and at least one photoconductive layer, said blocking layer having a surface resistivity greater than about 10^{10} ohms/square.

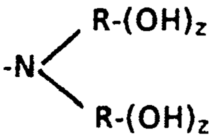
2. An electrophotographic imaging member according to Claim 1 wherein said vinyl hydroxy ester or vinyl hydroxy amide polymer is a polymeric reaction product of at least a monomer having the following structure:



wherein
X is selected from the group consisting of:

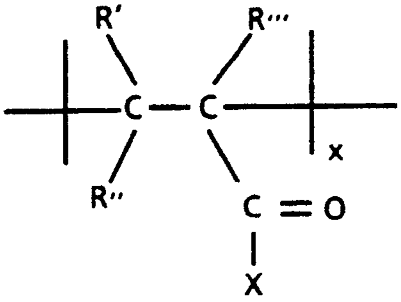
$-O-R-(OH)_z$, $-NH-R-(OH)_z$,

$-NR-R-(OH)_z$ and



R
is selected from the group consisting of aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms;
z
contains from 1 to 10 hydroxyl groups; and
R', R" and R'"
are independently selected from the group consisting of hydrogen, aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms.

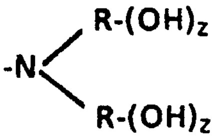
3. An electrophotographic imaging member according to Claim 1 wherein said vinyl hydroxy ester or vinyl hydroxy amide polymer is represented by the following formula:



wherein
x
represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000,
X
is selected from the group consisting of groups represented by the following groups:

$-O-R-(OH)_z$, $-NH-R-(OH)_z$,

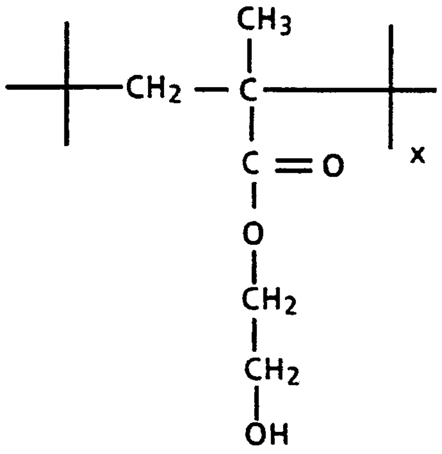
$-NR-R-(OH)_z$ and



R
is selected from the group consisting of aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms;
z
contains from 1 to 10 hydroxyl groups; and
R', R" and R'"
are independently selected from the group consisting of hydrogen, aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms.

4. An electrophotographic imaging member according to Claim 1 wherein said vinyl hydroxy ester

polymer is represented by the following formula:

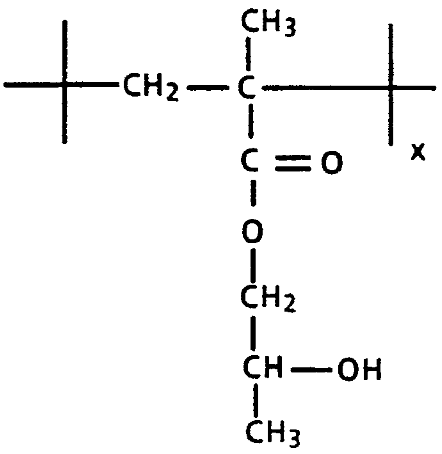


$$\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C(=O)-O-CH_2-CH_2-OH}{\overset{|}{\underset{|}{C}}}}- \right]_x$$

wherein x represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000.

5. An electrophotographic imaging member according to Claim 4 wherein said blocking layer has a thickness between about 0.8 micrometer and about 1 micrometer.

6. An electrophotographic imaging member according to Claim 1 wherein said vinyl hydroxy ester polymer is represented by the following formula:

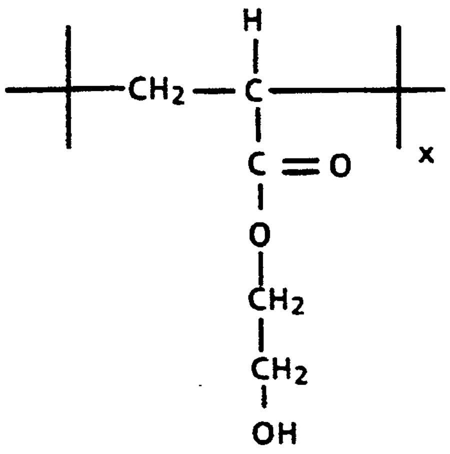


$$\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C(=O)-O-CH_2-CH(OH)-CH_3}{\overset{|}{\underset{|}{C}}}}- \right]_x$$

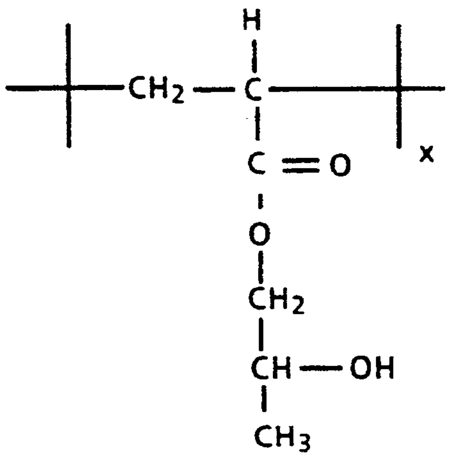
wherein x represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000.

7. An electrophotographic imaging member according to Claim 6 wherein said blocking layer has a thickness between about 0.8 micrometer and about 1 micrometer.

8. An electrophotographic imaging member according to Claim 1 wherein said vinyl hydroxy ester polymer is represented by a formula selected from the group consisting of:



and



wherein x represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000.

9. An electrophotographic imaging member according to Claim 1 wherein said vinyl hydroxy ester or vinyl hydroxy amide polymer has a weight average molecular weight of between about 20,000 and about 2,000,000.

10. An electrophotographic imaging member according to Claim 1 wherein said electrically conductive surface comprises carbon black impregnated polyvinyl fluoride and said blocking layer has a thickness between about 0.05 micrometer and about 8 micrometers.

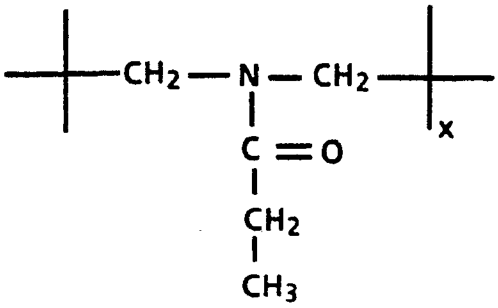
11. An electrophotographic imaging member according to Claim 1 wherein said blocking layer has a thickness between about 0.3 micrometer and about 1.5 micrometers.

12. An electrophotographic imaging member according to Claim 1 wherein said charge blocking layer comprises a blend of said hydroxylic polymer and another polymer miscible with said vinyl hydroxy ester or vinyl hydroxy amide polymer.

13. An electrophotographic imaging member according to Claim 12 wherein said vinyl hydroxy ester or vinyl hydroxy amide polymer comprises at least about 75 percent by weight of said blend.

14. An electrophotographic imaging member according to Claim 12 wherein said polymer miscible with said vinyl hydroxy ester or vinyl hydroxy amide polymer is represented by the following structural

formula:



$$\left[-CH_2-\underset{\underset{\underset{CH_3}{|}}{\underset{CH_2}{|}}}{\underset{\underset{|}{C=O}}{\underset{|}{N}}}-CH_2- \right]_x$$

wherein x represents sufficient repeat units for a molecular weight between about 20,000 and about 2,000,000.

15. An electrophotographic imaging member according to Claim 1 wherein said charge blocking layer comprises a copolymer comprising at least about 25 mole percent of said vinyl hydroxy ester or vinyl hydroxy amide repeat units.

16. An electrophotographic imaging member according to Claim 1 wherein said photoconductive layer comprises a charge generating layer and a charge transport layer.

17. An electrophotographic imaging member according to Claim 1 wherein said electrically conductive surface comprises a hole injecting material.

18. An electrophotographic imaging member according to Claim 17 wherein said electrically conductive surface comprises copper iodide.

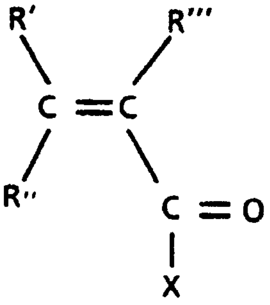
19. An electrophotographic imaging member according to Claim 1 wherein the resistivity of said electrically conductive surface is less than about 10^8 ohms/square.

20. An electrophotographic imaging member according to Claim 1 wherein an adhesive layer is sandwiched between said charge blocking layer and said photoconductive layer.

21. An electrophotographic imaging member according to Claim 20 wherein said adhesive layer comprises poly-4-vinylpyridine hydrogen bonded to said vinyl hydroxy ester or vinyl hydroxy amide polymer.

22. An electrophotographic imaging process comprising providing an electrophotographic imaging member having an imaging surface, said electrophotographic imaging member comprising a supporting substrate having an electrically conductive surface, a charge blocking layer comprising a vinyl hydroxy ester or vinyl hydroxy amide polymer, and at least one photoconductive layer, said blocking layer having a surface resistivity greater than about 10^{10} ohms/square, depositing a uniform electrostatic charge of at least about 20 volts/micrometer on said imaging surface, exposing said imaging member to activating radiation in image configuration to form an electrostatic latent image, contacting said imaging surface with marking particles to form a marking particle image on said imaging surface in conformance with said electrostatic latent image, transferring said marking particle image to a receiving member, and repeating said depositing, exposing, contacting and transferring steps at least once.

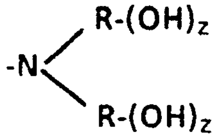
23. A process for preparing an electrophotographic imaging member comprising providing a supporting substrate having an electrically conductive surface, forming a dry, continuous charge blocking layer comprising a vinyl hydroxy ester or vinyl hydroxy amide polymer on said electrically conductive surface, and forming at least one photoconductive layer on said charge blocking layer, said vinyl hydroxy ester or vinyl hydroxy amide polymer being a polymeric reaction product involving at least a monomer having the following structure:



wherein
X is selected from the group consisting of:

$-O-R-(OH)_z$, $-NH-R-(OH)_z$

$-NR-R-(OH)_z$ and



$-N(R-(OH)_z)_2$

R
is selected from the group consisting of aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms;
z
contains from 1 to 10 hydroxyl groups; and
R', R'' and R'''
are independently selected from the group consisting of hydrogen, aliphatic, aromatic, heteroaliphatic, heteroaromatic, fused aromatic ring and heteroaromatic ring groups containing up to 10 carbon atoms.

24. A process for preparing an electrophotographic imaging member according to Claim 23 including wherein said forming of at least one photoconductive layer comprises applying a mixture of photoconductive particles dispersed in a solution of a film forming polymer dissolved in at least one solvent to form a coating and drying said coating to form a dry photoconductive layer.

25. A process for preparing an electrophotographic imaging member according to Claim 23 wherein said electrically conductive surface comprises a component that is soluble in a solvent in which said vinyl hydroxy ester or vinyl hydroxy amide polymer is substantially insoluble, and applying at least one coating solution subsequent to forming said blocking layer, said coating solution comprising said solvent.

26. A process for preparing an electrophotographic imaging member according to Claim 23 wherein said electrically conductive surface is insoluble in a lower alcohol, said vinyl hydroxy ester or vinyl hydroxy amide polymer is soluble in said lower alcohol, and applying at least one coating solution subsequent to forming said blocking layer, said coating solution comprising a solvent in which said conductive surface or component thereof is soluble or insoluble.

27. A process for preparing an electrophotographic imaging member according to Claim 23 including crosslinking said vinyl hydroxy ester or vinyl hydroxy amide polymer while forming said dry, continuous charge blocking layer comprising on said electrically conductive surface.

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EUROPEAN SEARCH REPORT

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EP 90 12 0917

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 274 (P-241)[1419], 7th December 1983; & JP-A-58 152 253 (CANON K.K.) 09-09-1983 * Abstract * ---	1-3,16	G 03 G 5/14
X	PATENT ABSTRACTS OF JAPAN, vol. 13, no. 162 (P-859)[3510], 19th April 1989; & JP-A-63 318 566 (RICOH CO., LTD) 27-12-1988 * Abstract * ---	1-4,8, 12,13	
X	US-A-4 822 705 (FUKAGAI et al.) * Abstract; column 11, lines 36-43,56-63; column 14, lines 8-12,16-19; column 13, lines 34-36 * ---	1,2,10-13,16, 23	
X	DE-A-3 006 740 (KONISHIROKU PHOTO) * Page 9, lines 4-5; page 10, lines 10-11 * ---	1,3,10, 11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
X	DE-A-3 325 443 (FUJI PHOTO FILM CO., LTD) * Abstract; page 9, lines 5,29-34; page 10, lines 6-8,19-23,36-37; page 11, line 11 * ---	1,2	G 03 G
X	DE-A-2 551 018 (KONISHIROKU PHOTO) * Page 2, line 26; page 4, line 25; page 8, examples 1-6; page 9, examples 7,8; page 29, claim 1 * -----	1-3	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-02-1991	VOGT C.H.C.

CATEGORY OF CITED DOCUMENTS

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