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[54] **PHOTOCONDUCTIVE ELEMENT WITH UNSAPONIFIED ALKYL VINYL ETHER-MALEIC ANHYDRIDE COPOLYMER INTERLAYER**

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[58] **Field of Search** 96/1.5, 1.6, 1.8

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[57] **ABSTRACT**

An electrophotographic photosensitive member comprises a support, a barrier layer overlying the support and comprising a high polymer such as nitrocellulose and an unsaponified alkylvinylether-maleic anhydride copolymer, and an organic photoconductive layer overlying the barrier layer.

6 Claims, No Drawings

PHOTOCONDUCTIVE ELEMENT WITH UNSAPONIFIED ALKYL VINYL ETHER-MALEIC ANHYDRIDE COPOLYMER INTERLAYER

This is a continuation, of application Ser. No. 230,129, filed Feb. 28, 1972, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an electrophotographic photosensitive member utilizing an organic photoconductive material.

2. Description of the Prior Art

Heretofore, there have been known various organic photoconductive materials of high polymer or low molecular weight such as poly-N-vinylcarbazole, brominated poly-N-vinylcarbazole, polyvinyl-anthracene, oxadiazoles, and acylhydrazones. When desired, sensitizers were added to the organic photoconductors to produce electrophotographic photosensitive members.

Organic photoconductive materials are excellent in points of transparency, flexibility, selectivity of charging polarity and surface smoothness. Particularly, high polymer organic photoconductive materials have film-shapeability.

However, a photosensitive member composed of an organic photoconductive material merely overlying a conductive support is not satisfactory to electrophotographic application since there occurs electrostatic trouble.

In other words, an electrophotographic photosensitive member comprising a conventional organic photoconductive material is often broken by discharging upon charging by corona discharging and the developed image contains white points which remarkably lower the image quality.

For the purpose of solving such drawback, it was proposed to provide a resin adhesive layer between an organic photoconductive layer and a support, but there is not yet obtained such a resin adhesive layer which does not lower the sensitivity of photosensitive layer and can sufficiently prevent discharging destruction.

In electrophotographic processes in which a photosensitive member is repeatedly used, there are various drawbacks, that is, fatigue phenomena such as lowering of the amount of charge, low uprising of charging, remaining memory and lowering of sensitivity as well as discharge destruction.

Heretofore, attempts have been made to apply a photosensitive member comprising an organic photoconductive material to an electrophotographic process using a photosensitive member repeatedly in charging, exposing, developing and transferring steps. Neither of the above mentioned problems was recognized.

A photosensitive member comprising a support and a photosensitive layer composed of ZnO-binder resin, and a barrier layer being provided therebetween is known, but a photosensitive member comprising a support and an organic photoconductive material, and a barrier layer being provided therebetween, is hardly used. Practically, effective barrier materials have not yet been found.

The present inventors have found particular barrier materials capable of preventing both discharge destruction and fatigue of a photosensitive member used for electrophotographic processes using the photosensitive member repeatedly.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided and electrophotographic photosensitive member which comprises a support, a barrier layer overlying the support and comprising a high polymer selected from the group consisting of nitrocellulose and copolymer of alkylvinylether and maleic anhydride, and an organic photoconductive layer overlying the barrier layer.

It is an object of this invention to provide an electrophotographic photosensitive member free from discharge destruction and causing fatigue phenomenon only to a less extent upon repeated use.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

A barrier layer used in this invention is to be selected in such a manner that the volume resistivity is of a certain appropriate value so as to completely prevent discharge destruction and, in a photosensitive member used repeatedly, the fatigue phenomenon is prevented and the barrier does not disadvantageously effect the electrophotographic characteristics, such as photosensitivity.

Barrier layer materials satisfying such requisites are nitrocellulose and copolymers of alkylvinylether and maleic anhydride.

There are various nitrocelluloses having various degrees of polymerization and degrees of nitration. These nitrocelluloses may be used for the present invention.

As alkylvinylether, there may be used methylvinylether, ethylvinylether, hexylvinylether, dodecylvinylether and the like. The higher the molecular weight of the alkylvinylether, the lower the copolymerizability with maleic anhydride and the film-shapeability. Therefore, alkyl having carbon atoms not exceeding 12 is preferable and that having carbon atoms not exceeding 6 is more preferable.

Providing such a barrier between an organic photoconductive layer and a support serves to prevent discharge destruction of the resulting photosensitive member and fatigue of the photosensitive member upon repeated use of the photosensitive member. Furthermore, such a barrier layer enables one to produce an electrophotographic photosensitive member having a photosensitive layer of excellent film characteristics such as adhesivity, flexibility, tensile strength and the like of stable performance.

As support used in this invention, there may be used various conventional supports used for electrophotographic photosensitive members. Representative supports are metal plates such as aluminum, copper and the like; paper; aluminum laminate paper; synthetic resin film containing surfactant; synthetic resin film treated with a quaternary ammonium salt for imparting conductivity; and glass, paper, and synthetic resin on which metal, metal oxide or metal halide is vapor-deposited. In general, surface resistivity is preferably less than 10^9 ohm and more preferably less than 10^5 ohm.

The barrier layer is formed on the support in such a manner that the barrier material such as nitrocellulose and copolymer of alkylvinylether and maleic anhydride is dissolved in an appropriate solvent and the viscosity is adjusted to such a value that is suitable for coating, and the resulting solution is coated on the support ac-

cording to conventional coating methods followed by drying such as air drying or heat drying to form a barrier layer.

Upon preparing the coating solution, a plasticizer mutually soluble with the barrier materials used in this invention may be added in an amount of 10–50 percent so as to improve the film property. The representative plasticizers are trichloroethyl phosphate, tricresylphosphate and diphenyl chloride. The resulting barrier layer film is satisfactrorily flexible, soft and of high strength.

The film thickness of the barrier layer is preferably less than about 10 microns, more preferably, 3–7 microns. When the thickness of barrier layer is thicker than 10 microns, some experiments show that the electrophotographic sensitivity is adversely affected. When the barrier layer is less than 10 microns thick, there is hardly recognized lowering of the sensitivity and when the barrier layer is thicker than 3 microns thick, discharge destruction and fatigue phenomenon upon repeated use of the photosensitive member can be prevented.

An organic photoconductive layer is formed on the barrier layer according to conventional methods to produce an electrophotographic photosensitive member of this invention.

As organic photoconductive materials, there may be used known organic photoconductive material. Particularly preferable materials are organic polymeric photoconductive materials such as poly-N-vinylcarbazole, chlorinated poly-N-vinylcarbazole, brominated poly-N-vinylcarbazole, cyanated poly-N-vinylcarbazole, polyvinylacenaphthene and the like.

Chlorinated poly-N-vinylcarbazole may be obtained by chlorinating poly-N-vinylcarbazole with chlorine gas or sulfuryl chloride, or by polymerizing a chlorinated vinylcarbazole. Detailed preparation methods are disclosed in German Offenlegungsschrift Pat. No. 2035679.

The following examples are given for illustrating the present invention, but not for restriction thereof.

EXAMPLE 1

An aqueous solution of an agent for lowering resistance poly-(N,N'-dimethyl-3, 5-methylene) piperidinium chloride was coated on a polyethyleneterephthalate film having an undercoating layer (75 microns thick) and dried to form a transparent conductive layer. Then, a 10 percent (by weight) solution of nitrocellulose (RS ½, trade name, supplied by Daiseru, degree of nitration of 11.5 – 12.2 percent) in a solvent composed of methyl ethyl ketone and acetone (7 : 3) was coated on the transparent conductive layer at a thickness of 3–4 microns (when dried) and dried to form a barrier layer. The resulting coating film (barrier layer) was highly transparent, strong and flexible and tightly adhered to the conductive layer. Futher, on the barrier layer was coated a photosensitive agent composed of poly-N-vinylcarbazole and benzene-chlorobenzene (1:1) at 8 g./m.^{2} and dried to form a photosensitive layer. The resulting transparent organic photoconductive film was subjected to a known electrophotographic reproduction procedure, that is, charging, exposing, reduction photographing, and wet-developing to form positive images. When the positive images were enlarged by a projector, it was found that the film was free from various electrostatic trouble and gave clear and sharp projected images. On the contrary, when a conventional photosensitive member having no barrier layer was used, there were formed a considerable number of white points caused by discharge destruction.

EXAMPLE 2

On a conductive layer, produced in a way similar to the procedure in Example 1, there was coated an 8 percent (by weight) solution of nitrocellulose (RS2, trade name, supplied by Daiseru, degree of nitration of 11.5–12.2 percent) in methyl ethyl ketone-methyl isobutyl ketone (6:4) at a thickness of 3–4 microns (when dried) to form a barrier layer. The resulting barrier layer showed excellent properties, similar to Example 1.

A solution composed of chlorinated poly-N-vinylcarbazole 3 g., N-vinylcarbazole 0.1 g., carbon tetrabromide 0.2 g., and benzene-chlorobenzene (1:1) was irradiated, stored in a dark place and coated on the barrier layer. The resulting transparent organic photoconductive film was treated in a way similar to that of Example 1. Thus, there was obtained excellent transparent positive images free from white points.

EXAMPLE 3

On a conductor composed of polyester film (75 microns thick) having an aluminum vapor deposited layer of visible ray transmitting rate of 60 percent there was coated 5 percent (by weight) solution of nitrocellulose (RS20, trade name, supplied by Daiseru, degree of nitration of 11.5–12.2 percent) in methyl ethyl ketone-methyl isobutyl ketone (6:4) to which 30 percent of trichloroethyl phosphate was added, at a thickness of 4–5 microns (when dried) to form a barrier layer. The resulting barrier layer was transparent, strong, flexible and highly adhesive to the deposited layer.

On the barrier layer there was coated a photosensitive agent composed of a solution of chlorinated poly-N-vinylcarbazole and Rhodamine B in benzene-chlorobenzene (1:1) at 5–6 g./m.^{2} and dried to produce a photosensitive layer.

The resulting photosensitive film was charged, exposed, reducing-photographed, and developed, in a way similar to that of Example 1, to produce sharp positive images. The sensitivity was very good. When the resulting positive images were enlarged with a projector, there were obtained projected images free from white points and of high fidelity to an original pattern. The film was strong, flexible and highly adhesive.

EXAMPLE 4

On a baryta paper subjected to a treatment for imparting conductivity there was coated a 10 percent (by weight) solution of nitrocellulose (SS ¼*a*, trade name, supplied by Daiseru, degree of nitration of 10.7–11.9 percent) in methanol-ethanol-toluene (7:2:1) of 15–20 microns thick (when dried) to form a barrier layer and dried. Further, on the resulting barrier layer there was coated a photosensitive agent composed of poly-N-vinylcarbazole and Crystal Violet in benzene-chlorobenzene (1:1) at 4–6 g./m.^{2} and dried. The resulting photosensitive paper was charged, exposed, and developed according to a conventional electrophotographic reproducing method to form clear visible images free from white points.

As is clear from the above mentioned result, an organic electrophotographic photosensitive member hav-

ing a barrier layer can overcome electrostatic trouble caused by discharging destruction and, in addition, the sensitivity was good and the physical properties of the coating were improved to a great extent. Therefore, according to the present invention, there can be produced a highly practical organic electrophotographic photosensitive member which is transparent or opaque.

EXAMPLE 5

On an aluminum plate (31 microns thick), conductive support, there was coated a 20 percent (by weight) solution of nitrocellulose (RS-1, trade name, supplied by Daiseru, degree of nitration of 11.5–12.2 percent) in methyl ethyl ketone-methyl isobutyl ketone (7:3) at 1–2 microns thick (when dried) and dried to form a barrier layer. The resulting barrier layer was highly transparent, strong and flexible, and tightly adhered to the aluminum support. On the barrier layer there was coated a photosensitive agent composed of poly-N-vinylcarbazole and Rhodamine B (molar ratio of $1:5 \times 10^{-5}$) and diphenyl chloride as plasticizer in benzene-monochlorobenzene (1:1) to form a photosensitive layer of 9 microns thick. For the purpose of using as a master for electrophotography, the resulting photosensitive plate was repeatedly subjected to an electrophotographic process which comprises corona-charging at −7.0 KV, exposing to a 500 W tungsten lamp at 40 lux. sec. and transferring the resulting electrostatic image to an electrostatic recording paper. When the electrostatic recording paper was developed with a liquid developer, the resulting image was excellent, and the effect of preventing discharge destruction was far better than by using conventional masters having no barrier layer. The durable repeating number was as shown below.

Having no barrier	about 100 times
Having a barrier	about 1000 times

EXAMPLE 6

A photosensitive plate prepared in a way similar to Example 5 was repeatedly subjected to a conventional xerographic process comprising charging at −7.0 KV, exposing about 100 lux. sec., developing with a liquid developer, transferring to an ordinary paper and cleaning the photosensitive plate. The sensitivity was excellent and the discharge destroy effect by the barrier layer was remarkable. The durable repeating number was as shown below.

Having no barrier	about 50 times
Having a barrier	about 500 times

EXAMPLE 7

On an aluminum plate (31 microns thick) a conductive support, there was coated a 6 percent (by weight) solution of nitrocellulose (RS40, trade name, supplied by Daiseru, degree of nitration 11.5–12.2 percent) in methyl ethyl ketone-methyl isolutyl ketone (7:3) at 1–2 microns thick (When dried) to form a barrier layer. This barrier layer had the same properties as those of Example 5.

On the barrier layer, there was coated a photosensitive agent composed of poly-N-vinylcarbazole and Crystal Violet (Molar ratio of $1:2.5 \times 10^{-5}$) and Coumarone RS ½ (trade name, supplied by Fuji Seitetsu) as a plasticizer in benzene-chlorobenzene (1:1) to form a photosensitive layer of about 8 microns thick. The resulting photosensitive plate was repeatedly subjected to a process for transferring an electrostatic image to an electrophotographic paper in a way similar to Example 5. The transferred electrostatic latent image was developed with a magnet brush. The discharge destroying preventing effect was remarkable, and the fatigue phenomenon was very little and the durable repeating number was as shown below.

Having no barrier layer	about 90 times
Having a barrier layer	about 1000 times

EXAMPLE 8

A photosensitive plate prepared in a way similar to Example 7 was repeatedly subjected to a conventional xerographic process comprising charging at −7.0 KV, exposing at 100 lux. sec., developing by a cascade method, transferring to an ordinary paper and cleaning the photosensitive plate. It was found that the discharge destroying preventing effect was excellent. The durable repeating number was as shown below.

Having no barrier	about 50 times
Having a barrier	about 500 times

EXAMPLE 9

On a support as used in Example 5 there was coated a 30 percent (by weight) solution of nitrocellulose (RS ½, trade name, supplied by Daiseru, degree of nitration of 11.5–12.2 percent) in methyl ethyl ketone-methyl isobutyl ketone (7:3) and dried to form a barrier layer of 1–2 microns thick. The resulting barrier layer was highly transparent, strong and flexible, and furthermore, could tightly adhere to aluminum as in case of Example 5.

On the barrier layer there was coated a photosensitive agent composed of 0.5 mole of chlorinated poly-N-vinylcarbazole and 2, 4, 7-trinitrofluorenone (molar ratio of 1:1) and diphenyl chloride as plasticizer in tetrahydrofuran to form a photosensitive layer of about 12 microns thick. The resulting photosensitive plate was repeatedly subjected to an electrostatic transferring method comprising charging at −7.0 KV, exposing at about 10 lux. sec., and transferring the resulting electrostatic image to electrostatic recording paper. When this electrostatic recording paper was developed with a liquid developer, the resulting image was good and there was observed the discharge destroying preventing effect. The durable repeating number was as shown below.

Having no barrier	about 300 times
Having a barrier	about 4000 times

EXAMPLE 10

An electrophotosensitive plate as used in Example 9 was repeatedly subjected to a xerographic process comprising charging at −7.0 KV, exposing at about 20 lux. sec., developing by a magnet brush method, transferring to an ordinary paper, and cleaning the photosensitive layer. The sensitivity was good and the discharge destroying preventing effect due to the barrier layer was remarkable. The durable repeating number was as shown below.

Having no barrier	about 200 times
Having a barrier	about 2000 times

EXAMPLE 11

On a sandblasted aluminum plate (100 microns thick) as as conductive support there was coated a barrier layer in a way similar to Example 5. On the barrier layer there was coated a photosensitive agent composed of 0.5 mole of chlorinated poly-N-vinylcarbazole and Rhodamine B (molar ratio of $1:5 \times 10^{-5}$) and 0.5 g. of diphenyl chloride as plasticizer in benzene-chlorobenzen (1:1) at 4 microns thick (when dried).

The resulting photosensitive plate was repeatedly subjected to an electrostatic transferring process comprising charging at −7.0 KV, exposing at about 40 lux. sec., and transferring to an electrostatic recording paper. The electrostatic recording paper was developed with a liquid developer. The discharge destroying preventing effect was remarkably improved. The durable repeating number was as shown below.

Having no barrier layer	about 100 times
Having a barrier layer	about 1000 times

EXAMPLE 12

On a paper treated for imparting conductivity as a conductive support there was coated a 10 percent (by weight) solution of nitrocellusose (RS2, trade name, supplied by Daiseru, degree of nitration of 11.5–12.2 percent) in methyl ethyl ketone-methyl isobutyl ketone (7:3) at 1–2 microns thick (when dried) to form a barrier layer. The resulting barrier layer has film properties similar to that of Example 5. On the barrier layer there was coated a photosensitive agent composed of 0.5 mole of chlorinated poly-N-vinylcarbazole and 2, 4, 7-trinitrofluorenone (molar ratio of 1:1) and 0.5 g. of diphenyl chloride in tetrahydrofuran at about 12 microns thick. This photosensitive plate was repeatedly subjected to an electrostatic transferring method comprising charging at −7.0 KV, exposing at about 5 lux. sec. and transferring to an electrostatic recording paper. The electrostatic recording paper was developed by a magnet brush method to produce images of good quality. The discharge destroying preventing effect was also excellent. The durable repeating number was as shown below.

Having no barrier	about 200 times
Having a barrier	about 3000 times

EXAMPLE 13

On a conductive member composed of polyester film (75 microns thick) having an aluminum vapor-deposited layer having a visible ray transmittance rate of 60 percent, there was coated a 10 percent (by weight) solution of nitrocellulose (RS20, trade name, supplied by Daiseru, degree of nitration of 11.5–12.2 percent) in methyl ethyl ketone- methyl isobutyl ketone (7:3) at 1–2 microns thick (when dried) to form a barrier layer. This barrier layer had film properties similar to that of Example 5. Further, on the barrier layer there was coated a photosensitive agent composed of poly-N-vinylcarbazole and Crystal Violet (molar ratio of $1:2.5 \times 10^{-5}$) and 0.5 g. of diphenyl chloride as phosticizer in benzene-chloro-benzene (1:1) at about 4 microns thick (when dried).

The resulting photosensitive member was repeatedly subjected to an electrostatic transferring method comprising charging at −7.0 KV, exposing at about 100 lux. sec. and transferring to an electrostatic recording paper. The electrostatic recording paper was developed with a liquid developer. The discharge destroying preventing effect was remarkable.

EXAMPLE 14

On a polyethyleneterephthalate film (75 microns thick) there was coated, as an undercoating, an aqueous solution of poly-(N, N'-dimethyl-3,5-methylene) piperidinium chloride, and an agent for imparting conductivity, and dried to produce a transparent conductive layer. On the resulting undercoating there was coated a 10 percent (by weight) solution of an unsaponified methylvinylether-maleic anhydride copolymer (GANTREZ. AN-139, trade name, supplied by GAF co.) in ethyl acetate-butyl acetate (7:3) at 3–4 microns thick and dried to form a barrier layer. The resulting coating was highly transparent, strong, and flexible, and could tightly adhere to the conductive layer.

On the barrier layer, there was coated a photosensitive agent composed of poly-N-vinyl-carbazole and Crystal Violet in benezene-chlorobenzene (1:1) at 8–10 g./m.^{2} and dried to form a photosensitive layer. The resulting transparent organic photoconductive film was subjected to a conventional electrophotographic reproduction process comprising charging, exposing, reduction-photographed, developing with a liquid developer.

The resulting positive image was of high quality. When this image was enlarged by a projector, a clear projected image was obtained, and the film according to the present invention was free from electrostatic trouble.

On the contrary, a conventional photosensitive member having no barrier layer, i.e., a photosensitive layer directly overlying a conductive layer, gave white points caused by discharge destruction.

EXAMPLE 15

On a conductive layer as obtained in Example 14, there was coated an 8 percent (by weight) solution of methylvinylether-maleic anhydride copolymer (PVM/MA, trade name supplied by Mitsubishi Kasei, high viscosity) in methyl ethyl ketone at 4–5 microns thick (when dried) to form a barrier layer. The resulting barrier layer showed good properties, similar to that of Example 14.

A solution of chlorinated poly-N-vinylcarbazole 3 g., N-vinylcarbazole 0.1 g. and carbon tetrabromide 0.2 g. in benzene-chlorobenzene (1:1) was irradiated with ultraviolet ray and kept in a dark place and then applied onto the surface of the barrier layer. The resulting transparent organic photoconductive film was treated in a way similar to that of Example 14 to produce a transparent positive image free from white points.

EXAMPLE 16

On a transparent conductive layer of polyester film (75 microns thick) having an aluminum vapor-deposited layer of visible ray transmitting rate of 60 percent there was coated a 7.5 percent (by weight) solution of an unsaponified methylvinylether-maleic anhydride copolymer (GANTREZ AN-149, trade name, supplied by GAF co.) in ethyl acetate-butyl acetate-methyl ethyl ketone (7:2:1) to which 30 percent of trichloroethylphosphate was added, at 4–5 microns (when dried) and dried to form a barrier layer. The resulting barrier layer was transparent, strong, flexible and adhered tightly to the vapor-deposited layer as in Example 14.

On the barrier layer there was coated a photosensitive agent composed of chlorinated poly-N-vinylcarbazole and Rhodamine B in benzene-chlorobenzene (1:1) at 5–6 g./m.^{2} and dried to form a photosensitive layer. The resulting transparent organic photoconductive film was subjected, in a way similar to Example 14, to charging, exposing, reduction-photographing and developed with a liquid developer to form a positive image of high sensitivity and good quality. When the resulting image was enlarged by a projector, there was obtained a projected image free from white points caused by discharge destruction and of high fidelity to the original pattern. Furthermore, the above mentioned film was strong, flexible and adhered tightly.

EXAMPLE 17

On a baryta paper treated for imparting conductivity there was coated an 8 percent (by weight) solution of butylvinylether-maleic anhydride copolymer in ethyl acetate-methyl ethyl ketone-butyl acetate (7:1:2) at 4–5 microns thick and dried to form a barrier layer. Further, on the barrier layer there was coated a photosensitive agent composed of poly-N-vinylcarbazole and Crystal Violet in benzene-chlorobenzene (1:1) at 6 g./m.^{2} and dried. The resulting photosensitive paper was subjected to a conventional electrophotographic reproductive method comprising charging, exposing, and developing to form a clear visible image, and no white points were observed.

EXAMPLE 18

Following the procedure of Example 17, by using dodecylvinylether-maleic anhydride copolymer in place of hexylvinylether-maleic anhydride copolymer, there was obtained a result almost similar to Example 17.

EXAMPLE 19

On an aluminum plate (31 microns thick) conductive support, there was coated a 20 percent (by weight) solution of an unsaponified methylvinylether-maleic anhydride copolymer (GANTREZ AN-139, trade name, supplied by GAF Co.) in ethyl acetate-butyl acetate (7:3) at 1–2 microns thick (when dried) and dried to form a barrier layer. The resulting barrier layer was transparent, strong, flexible and adhered tightly to the aluminum support. Further, on the barrier layer there was coated a photosensitive agent composed of poly-N-vinylcarbazole and Rhodamine B (molar ratio of 1:5 × 10^{-5}) and diphenyl chloride in benzene-monochlorobenzene (1:1) to form a photosensitive layer of 9 microns thick. For the purpose of using the resulting photosensitive plate as an electrophotographic master, the photosensitive plate was repeatedly subjected to an electrostatic latent image transferring method comprising corona-charging at −7.0 KV, exposing to a 500 W tungsten lamp at 40 lux. sec. and transferring the electrostatic latent image to an electrostatic recording paper. The electrostatic recording paper was developed with a liquid developer to form a visible image of good quality. The discharge destroying preventing effect was far greater than that of a conventional master having no barrier layer. The durable repeating member was as shown below.

Having no barrier layer	about 50 times
Having a barrier layer	about 300 times

EXAMPLE 20

A photosensitive plate prepared in a way similar to Example 19 was repeatedly subjected to a conventional xerographic process comprising charging at −7.0 KV, exposing at 100 lux. sec., developing with a liquid developer, transferring to an ordinary paper, and cleaning to photosensitive plate. The sensitivity was good and the discharge destroying preventing effect was remarkable. The durable repeating number was as shown below.

Having no barrier layer	about 40 times
Having a barrier layer	about 400 times

EXAMPLE 21

On an aluminum plate (31 microns thick) conductive support, there was coated a 6 percent (by weight) solution of methylvinyl-ether-maleic anhydride copolymer (PVM/MA, trade name, supplied by Mitsubishi Kasei) in ethyl acetate-butyl acetate (7:3) at 1–2 microns thick to form a barrier layer. This barrier layer had properties similar to Example 19. On the resulting barrier layer there was coated a photosensitive agent composed of poly-N-vinylcarbazole and Crystal Violet (molar ratio of 1:2.5 × 10^{-5}) and Coumarone RS ½ (trade name, supplied by Fuji Seitetsu) as a plasticizer

in benzene-chlorobenzene (1:1) to form a photosensitive layer of about 8 microns thick. The resulting photosensitive plate was repeatedly subjected to the same process as in Example 19 comprising transferring electrostatic images to an electrostatic recording paper. The electrostatic latent image transferred was developed with a magnet brush. The discharge destroying preventing effect was excellent, and fatigue phenomenon was very little. The durable repeating number was as shown below.

Having no barrier layer	about 50 times
Having a barrier layer	about 3000 times

EXAMPLE 22

A photosensitive plate prepared in a way similar to Example 21 was repeatedly subjected to a conventional xerographic process comprising charging at −7.0 KV, exposing at about 100 lux. sec., developing by a cascade method, transferring to an ordinary paper, and cleaning the photosensitive plate. The discharge destroying preventing effect was very good. The durable repeating number was as shown below.

Having no barrier layer	about 50 times
Having a barrier layer	about 3000 times

EXAMPLE 23

On a support as used in Example 19 there was coated a 30 percent (by weight) solution of hexylvinylether-maleic anhydride copolymer in methyl ethyl ketone and dried to form a barrier layer of 1–2 microns thick. The resulting barrier layer was transparent, strong, flexible and adhered tightly to aluminum.

On the barrier layer there was coated a photosensitive agent composed of 0.5 mole of chlorinated poly-N-vinylcarbazole and 2, 4, 7-trinitro fluorenone (molar ratio of 1:1) and diphenyl chloride as plasticizer in tetrahydrofuran to form a photosensitive layer of about 12 microns thick. The resulting photosensitive plate was repeatedly subjected to an electrostatic transferring process comprising corona-charging at −7.0 KV, exposing at about 10 lux. sec., and transferring an electrostatic latent image to an electrostatic recording paper. The electrostatic latent image was developed with a liquid developer. The visible image thus developed was good and the discharge destroying preventing effect was observed. The durable repeating number was as shown below.

Having no barrier layer	about 200 times
Having a barrier layer	about 4000 times

EXAMPLE 24

A photosensitive plate similar to that of Example 23 was repeatedly subjected to a xerographic process comprising charging at −7.0 KV, exposing at about 20 lux. sec., developing by a magnet brush method, transferring to an ordinary paper and cleaning the photosensitive layer. The sensitivity was good and the discharge destroying preventing effect was remarkably good. The durable repeating number was as shown below.

Having no barrier layer	about 200 times
Having a barrier layer	about 3000 times

EXAMPLE 25

A barrier layer was formed on a sandblasted aluminum plate of 100 microns thick as a conductive support in a way similar to Example 19. On the barrier layer there was coated a photosensitive agent composed of 0.5 mole of chlorinated poly-N-vinylcarbazole and Rhodamine B (molar ratio of $1:5 \times 10^{-5}$) and 0.5 g. of diphenyl chloride as plasticizer in benzene-chlorobenzene (1:1) at 4 microns thick (when dried). The resulting photosensitive plate was repeatedly subjected to an electrostatic transferring method comprising charging at −7.0 KV, exposing at about 40 lux. sec. and transferring to an electrostatic recording paper. The electrostatic recording paper was developed with a liquid developer. The discharge destroying preventing effect was markedly improved. The durable repeating number was as shown below.

Having no barrier layer	about 150 times
Having a barrier layer	about 2000 times

EXAMPLE 26

On a paper, having a surface which was treated for imparting electroconductivity, as a conductive support, there was coated a 10% (by weight) solution of methylvinylether-maleic anhydride copolymer (Gantrez. AN-179, trade name, supplied by GAF Co.) in ethyl acetate-butyl acetate (7:3) at 1–2 microns thick (when dried) to form a barrier layer. The resulting barrier had film properties similar to those of Example 19. On the barrier there was coated a photosensitive agent composed of 0.5 mole of chlorinated poly-N-vinylcarbazole and 2, 4, 7-trinitrofluorenone (molar ratio of 1:1) and 0.5 g. of diphenyl chloride as plasticizer in tetrahydrofuran at about 12 microns thick. The photosensitive plate was repeatedly subjected to an electrostatic transferring method comprising charging at −7.0 KV, exposing at about 5 lux. sec. and transferring to an electrostatic recording paper. The electrostatic recording paper was developed by a magnet brush method to produce visible images of good quality. The discharge destroying preventing effect was also good. The durable repeating number was as shown below.

Having no barrier layer	about 200 times
Having a barrier layer	about 6000 times

EXAMPLE 27

On a polyester film (75 microns thick) having an alu-

minum vapor-deposited layer of visible ray transmitting rate of 60 percent, a conductive member, there was coated as a 10 percent (by weight) solution of dodecylvinylether-maleic anhydride copolymer in methyl ethyl ketone at 1–2 microns thick (when dried) to form a barrier layer. The resulting barrier layer had film properties similar to those of Example 19. On the barrier layer there was coated a photosensitive agent composed of poly-N-vinylcarbazole and Crystal Violet (molar ratio of $1:2.5 \times 10^{-5}$) and 0.5 g. of diphenyl chloride as plasticizer in benzene-chlorobenzene (1:1) at about 4 microns thick (when dried).

The resulting photosensitive plate was repeatedly subjected to an electrostatic transferring method comprising charging at −7.0 KV, exposing at about 100 lux. sec. and transferring to an electrostatic recording paper. The electrostatic recording paper was developed with a liquid developer. The discharge destroying preventing effect was remarkable. The durable repeating number was as shown below.

Having no barrier layer	about 100 times
Having a barrier layer	about 5000 times

We claim:

1. An electrophotographic photosensitive member comprising a support whose surface resistivity is less than 10^9 ohms, overlying the support an intermediate layer less than 10 microns thick for preventing electric deterioration and fatigue phenomena due to repeated uses, said intermediate layer consisting essentially of an unsaponifed copolymer of an alkylvinylether and maleic anhydride, in which the number of carbon atoms in the alkyl radical of said alkylvinylether is 1–12 and a photoconductive layer, overlying said intermediate layer, said photoconductive layer consisting essentially of an organic photoconductive material.

2. An electrophotographic photosensitive member according to claim **1**, wherein said alkylvinylether is selected from the group consisting of methylvinylether, ethylvinylether, hexylvinylether, and dodecyvinylether.

3. An electrophotographic photosensitive member according to claim **1**, wherein the number of carbon atoms of the alkyl radical of said alkylvinylether is 1–6.

4. An electrophotographic photosensitive member comprising a support whose surface resistivity is less than 10^9 ohms, overlying the support an intermediate layer less than 10 microns thick for preventing electric deterioration and fatique phenomena due to repeated uses, said intermediate layer consisting essentially of (1) an unsaponifed copolymer of an alkylvinylether and maleic anhydride, in which the number of carbon atoms in the alkyl radical of said alkylvinylether is 1–12, and (2) a mutually soluble plasticizer, and a photoconductive layer overlying said intermediate layer, said photoconductive layer consisting essentially of an organic photoconductive material.

5. An electrophotographic photosensitive member according to claim **4** wherein said plasticizer is present in an amount between about 10 percent to about 50 percent by weight.

6. An electrophotographic photosensitive member according to claim **5** wherein said plasticizer is selected from the group consisting of trichloroethyl phosphate, tricresylphosphate and diphenyl chloride.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,860,422 Dated January 14, 1975

Inventor(s) HIROSHI MATSUNO, ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 29, insert --a-- between "coated" and "5"

Column 5, line 62, delete "a";

Column 7, line 27,"as as" should read --as a--;

line 52, "nitrocellusose" should read

--nitrocellulose--

Column 12, lines 41-42 "Gantrez" should read --GANTREZ--

Column 14, line 17, "fatique" should read --fatigue--

Signed and sealed this 15th day of April 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

FORM PO-1050 (10-69)

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