



EUROPEAN PATENT APPLICATION

Application number : **92310645.4**

Int. Cl.⁵ : **G03G 5/14, G03G 5/147**

Date of filing : **20.11.92**

Priority : **22.11.91 JP 307990/91**

Date of publication of application :
26.05.93 Bulletin 93/21

Designated Contracting States :
CH DE FR GB IT LI

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Electrophotographic method and photosensitive material used therefor.

An electrophotographic method which uses a photosensitive material which has a photosensitive layer and a surface protecting layer that are formed on an electrically conducting substrate, wherein the surface protecting layer is a varistor-type surface protecting layer having non-linear voltage-current characteristics, and the photosensitive material is electrically charged under a condition wherein an electric field of the surface protecting layer is smaller than a threshold electric field thereof and is exposed to light to remove electricity under a condition where the electric field of the surface protecting layer is greater than the threshold electric field thereof. This method makes it possible to obtain a vivid image maintaining improved electrostatic repetitive characteristics and photosensitivity without permitting the photosensitive material to lose corona charging characteristics.

Background of the Invention

1. Field of the Invention

5 The present invention relates to an electrophotographic method employed for a copying machine, a laser printer and the like, and to a surface-protected photosensitive material used therefor. More specifically, the invention relates to an electrophotographic method which makes it possible to obtain excellent photosensitivity and vividness in the image without losing corona charging characteristics and which further exhibits markedly improved electrostatic repetitive characteristics, and a surface-protected photosensitive material used there-
10 for.

2. Description of the Prior Art

A photosensitive material used for the electrophotographic method can be represented by a function separated-type laminated photosensitive material which is obtained, for example, by laminating an electric charge generating layer (CGL) and an electric charge transporting layer (CTL) in this order on an electrically conducting substrate or, conversely, by laminating the electric charge transporting layer (CTL) and the electric charge generating layer (CGL) in this order on the electrically conducting substrate.

Among these laminated photosensitive materials, the latter one has an advantage in that positive electric charging can be accomplished while permitting ozone to generate little accompanied, however, by defects of poor abrasion resistance in mechanical (physical) sense and in chemical sense since the layer of generating electric charge is positioned on the outermost surface. In order to prevent this defect, therefore, a surface protecting layer (CGL) has generally been provided on the layer of generating electric charge.

The surface protecting layers include those of the electrically insulating type, those of the low resistance type, those of the electron transporting type, and the like. For instance, Japanese Laid-Open Patent Publication No. 30846/1982 discloses a photosensitive material obtained by providing on a photoconducting layer a protecting layer in which a fine metal oxide powder is dispersed in a binder resin. Japanese Patent Publication No. 40311/1988 discloses the use of a metal oxide which contains both a tin oxide and an antimony oxide. Moreover, Japanese Patent Publication No. 3171/1990 discloses the use of the fine metal oxide powder having an average grain size of smaller than 0.3 μm at a ratio of 40 to 90% by weight in the protecting layer.

Among those of the above prior art, the one which uses an electrically insulating surface protecting layer permits the material to be selected from a wide range and can be designed relatively easily. In order to prevent the reduction in the electrostatic characteristics of the photosensitive layer, however, the thickness of the surface protecting layer must be reduced to a considerable degree (about 5 μm), making it difficult to obtain both
35 the function of the protecting layer itself and the function inherent in the electrophotographic photosensitive member.

Furthermore, the surface protecting layer of electron transportation type contains an electron transporting substance therein and receives the electrons that are formed by light in the photosensitive layer, and transports the electrons up to the surface of the protecting layers in order to neutralize the corona positive charging. Under
40 the present circumstances where no excellent electron transporting substance has yet been developed, however, the surface protecting layer of the electron transporting type cannot be put to the practical use at least for the time being.

According to the surface protecting layer of the above low resistance type, furthermore, an electrically conducting substance is contained in large amounts in the protecting layer in order to decrease the volume resistivity to smaller than $10^{14} \Omega\text{-cm}$ and, particularly, to 10^{13} to $10^{11} \Omega\text{-cm}$, in an attempt to store the electric charge given by the corona discharge not in the surface of the protecting layer but in the interface between the protecting layer and the photosensitive layer to render it electrically charged, such that the electric charge of an opposite polarity generated on the surface of the photosensitive layer is discharged more quickly. In this case, however, another intermediate layer, i.e., a blocking layer must be provided to trap the electric charge
50 in the interface between the protecting layer and the photosensitive layer, in order to maintain stability in electric charging. Moreover, since the electrostatic latent image is formed not on the surface of the protecting layer but on the underlying interface, there arise such problems as a reduction in the resolution during the toner developing and a so-called image flow since the surface layer has a small electric resistance.

55 Summary of the Invention

The object of the present invention, therefore, is to provide an electrophotographic method which is free the above-mentioned defects inherent in the conventional surface protecting members, which makes it pos-

sible to obtain excellent photosensitivity and vividness in the image without losing corona charging characteristics and which further exhibits markedly improved electrostatic repetitive characteristics, and to provide an electrophotosensitive material.

Another object of the present invention is to provide a novel electrophotographic method which utilizes such characteristics that when dark, the surface protecting layer assumes a large resistance and is stably charged and when bright (when exposed to light), the surface protecting layer loses its resistance and permits the electrons to be transported, and to provide a surface-protected photosensitive material used for this method.

According to the present invention, there is provided an electrophotographic method which uses a photosensitive material obtained by providing a photosensitive layer and a surface protecting layer on an electrically conducting substrate, wherein said surface protecting layer on an electrically conducting substrate, wherein said surface protecting layer comprises a varistor-type surface protecting layer having non-linear voltage-current characteristics, said photosensitive material is electrically charged under a condition where the electric field of the surface protecting layer is smaller than a threshold electric field thereof, and said photosensitive material is exposed to light to remove electricity under a condition where the electric field of the surface protecting layer is greater than the threshold electric field thereof.

According to the present invention, furthermore, there is provided a surface-protected photosensitive material for electrophotography obtained by providing a photosensitive layer and a surface protecting layer on an electrically conducting substrate, wherein said surface protecting layer comprises a varistor-type surface protecting layer having non-linear voltage current characteristics.

The surface protecting layer used for the present invention should have varistor-type characteristics, i.e., non-linear voltage-current characteristics, and should have a threshold electric field which is greater than 2×10^5 V/cm and, particularly, which lies over a range of from 4×10^5 to 1×10^6 V/cm, and a voltage non-linear coefficient (b) defined by the equation (1)

$$I = a \cdot V^b \quad (1)$$

where I is a current, V is a voltage, a is a proportional constant, and b is a non-linear voltage coefficient, which is greater than 3 and, particularly, which lies over a range of from 5 to 50.

The surface protecting layer comprises, for instance, a thermosetting resin and an electrically conducting fine powder that is dispersed in the above resin in an amount of 10 to 40% by weight and, particularly, 20 to 30% by weight with respect to the total amount, and has a volume resistivity which is greater than $1 \times 10^{14} \Omega\text{-cm}$ as measured in an electric field which is lower than the threshold electric field, for example, as measured in an electric field of 1×10^5 V/cm. In particular, the surface protecting layer comprises a resin composition having a volume resistivity which lies over a range of from 1×10^{15} to $1 \times 10^{17} \Omega\text{-cm}$. In this resin composition, the electrically conducting fine powder should be dispersed maintaining an average particle-to-particle distance of 100 to 500 Å as measured by using an electron microscope.

The present invention can be adapted to a photosensitive material having any photosensitive layer, and presents a distinguished advantage particularly for a laminated photosensitive material of the positively charging type in which the photosensitive layer consists of a laminate of an electric charge transporting layer of the side of the electrically conducting substrate and an electric charge generating layer of the side of the surface protecting layer. In this case, the electrically conducting fine powder should have an electron energy level which is higher by 0.05 to 1.00 eV than that of the electric charge generating substance in the electric charge generating layer.

According to the present invention, the surface protecting layer comprises a photosensitive material having a varistor-type surface protecting layer which has non-linear voltage-current characteristics, the photosensitive material is electrically charged under a condition where the electric field of the surface protecting layer is smaller than a threshold electric field thereof, and the photosensitive material is exposed to light to remove electricity under a condition where the electric field of the surface protecting layer is greater than the threshold electric field thereof. When dark, therefore, the surface protecting layer assumes a large resistance and is stably charged and when bright, the surface protecting layer loses its resistance and permits the electric charge on the surface to be effectively removed, making it possible to obtain excellent photosensitivity, vividness of image and high contrast without impairing corona charging characteristics. It is further allowed to markedly improve abrasion resistance as well as repetitive characteristics such as effectively reducing the residual potential while maintaining a high initial potential.

Brief Description of the Drawings

Fig. 1 is a graph illustrating relationships between the applied voltage and the current density of a surface protecting layer used in the present invention;

Fig. 2 is a diagram explaining the principle of the present invention, wherein the diagram A shows a step of electric charging and the diagram B shows a step of exposure to light to remove electricity;

Fig. 3 is a graph showing the surface potential of when the surface-protected photosensitive material is electrically charged and is exposed to light; and

Fig. 4 is a graph showing the number of repetition of electric charging and exposure to light to remove electricity, and a relationship between the effective initial potential and the residual potential of the exposed portion.

Detailed Description of the Invention

According to the present invention, a first feature resides in the use of a photosensitive material provided with a varistor-type surface protecting layer having non-linear voltage-current characteristics as a surface protecting layer.

The varistor is defined as a non-linear resistor which is susceptible to a change in the voltage. That is, the varistor stands for an element which, under a certain threshold voltage condition, exhibits a very large resistance and permits very little current to flow but which, when the threshold voltage is exceeded, exhibits a resistance that decreases abruptly to permit the current to flow.

In Fig. 1 are plotted relationships between the applied voltage (V) and the current density (A/cm²) of a surface protecting layer (for details, refer to Example 1 appearing later) that is used in the present invention, and wherein a curve A represents the results of measurement of when the above layer is interposed between an aluminum foil and a stainless steel plate, and a curve B represents the results of measurement of when the above layer is interposed between the electric charge generating layer on the aluminum foil and the stainless steel plate.

According to Fig. 1, the current does not almost flow in either case so far as the applied voltage is smaller than a threshold voltage V_{cr} . The current, however, increases exponentially as the applied voltage becomes greater than the threshold voltage.

Referring to Fig. 1, furthermore, the surface protecting layer (B) which has the varistor layer provided between the conductors via a charge generating layer exhibits a threshold voltage (V_{cr}) which is twice or more greater than that of the surface protecting layer (A) which has the varistor layer that is simply provided between the conductors, and exhibits the effect for enhancing the threshold voltage though the thickness is increased by the provision of the charge generating layer.

In the electrophotographic method of the present invention, another distinguished feature resides in that use is made of a photosensitive material which has a varistor-type surface protecting layer formed on the photosensitive layer, and the photosensitive material is electrically charged under a condition where the electric field of the surface protecting layer is smaller than a threshold electric field thereof, and is exposed to light to remove electricity under a condition where the electric field of the surface protecting layer is greater than the threshold electric field thereof.

That is, when a voltage is applied to the photosensitive material under dark condition, the surface protecting layer is placed in an electric field which is smaller than a threshold value thereof and assumes a high resistance. Therefore, the surface is stably charged to a high potential. When bright (exposed to light to remove electricity), on the other hand, there is established a large electric field in excess of the threshold electric field due to carriers (electric charge of opposite polarity) formed excessively by light on the surface of the photosensitive layer and the electric charge on the surface of the surface protecting layer. Therefore, the surface protecting layer loses electric resistance, and whereby the electric charge moves to the interface of the photosensitive layer passing through the surface protecting layer. As a result, increased photosensitivity and increased contrast are obtained without impairing the charging characteristics.

To explain the principle of the electrophotographic method of the present invention, Fig. 2 shows a preferred photosensitive material, wherein the diagram A shows a step of electric charging and the diagram B shows a step of exposure to light to remove electricity. The photosensitive material 1 comprises an electrically conducting substrate 2, an electric charge transporting layer (a positive hole transporting layer) 3 formed on the electrically conducting substrate, an electric charge generating layer 4 formed on the electric charge transporting layer, and a varistor-type surface protecting layer 5 formed on the electric charge generating layer.

In the step A of electric charging, the surface of the photosensitive material is positively charged using a positive corona charging mechanism 6. Therefore, the surface of the varistor-type surface protecting layer 5 is positively charged with a constant voltage V_s depending on a saturation charging potential and a dark attenuation factor. According to the present invention, the electric charging is effected in a manner that the electric field E of the varistor-type surface protecting layer 5 is smaller than a threshold electric field E_{cr} thereof. The electric field intensity E_0 applied to the surface protecting layer is approximately given by the following

equation (2)

$$E_0 \doteq \frac{V_s}{t_p + t_0} \leq E_{cr} \quad (2)$$

where t_0 denote a thickness of the photosensitive layer (thickness of the electric charge transporting layer + electric charge generating layer), and t_0 denotes a thickness of the varistor-type surface protecting layer.

Then, in the step of exposure to light to remove electricity, the photosensitive material after electrically charged is exposed to the light of image using an image exposing mechanism 7. As a result of exposure to the light of image in the bright portion L, positive holes of the electric charge formed by light in the electric charge generating layer 4 are quickly neutralized by the mirror image electric charge (negative polarity) of the substrate electrode due to the action of the electric charge transporting layer 3. However, since the electrons stay excessively in the electric charge generating layer 4, the electric field intensity E_1 applied to the surface protecting layer is approximately expressed by the equation (3)

$$E_1 \doteq \frac{V_s}{t_0} \quad (3)$$

Since the thickness t_0 of the surface protecting layer is considerably smaller than the resultant thickness $t_p + t_0$ of the photosensitive layer and the surface protecting layer, it is allowed to effect the electric charging and removal of electricity to a degree to fully satisfy the equation (4)

$$E_1 > E_{cr} \geq E_0 \quad (4)$$

It is therefore allowed to pour the electrons from the photosensitive layer into the surface protecting layer 5 and to transport the electrons in the surface protecting layer to a sufficient degree, thereby to sufficiently neutralize the positive electric charge in the surface.

In a dark portion D of the photosensitive material, the surface maintains a sufficiently high potential and exhibits a sufficiently high electric resistance. It is therefore allowed to form through developing an image of a high concentration maintaining excellent resolution and contrast.

Fig. 3 illustrates the surface potential at the time of electric charging and exposure to light.

According to the present invention, use of the varistor-type surface protecting layer makes it possible to prevent the accumulation of residual potential in the exposed portion L when the electric charging and exposure to light to remove electricity are carried out repetitively, as well as to suppress the drop in the initial saturation potential, which are quite unexpected effects. Fig. 4 is a diagram plotting relationships among the number of times of repetition of electric charging and exposure to light to remove electricity along the abscissa, and the effective initial potential and residual potential in exposed portion along the ordinate. Broken lines represent values of the photosensitive material of when an ordinary electrically insulating resin is used as the surface protecting layer, and solid lines represent values of the photosensitive material of when the varistor-type surface protecting layer is used in accordance with the present invention. It will be obvious from Fig. 4 that when used repetitively, the conventional surface-protected photosensitive material exhibits an increase in the residual potential due to the trapping of electric charge and a decrease in the effective surface potential. According to the present invention, on the other hand, these tendencies are almost all eliminated.

According to the present invention, the threshold electric field of the varistor-type surface protecting layer that lies within the above-mentioned range is important for improving the electrically charging property and for holding the electric charge in the surface of the surface protecting layer, and the nonlinear voltage coefficient that lies within the above range is important for increasing the photosensitivity and for decreasing the residual potential. With the varistor-type surface protecting layer satisfying the above requirements being provided on the photosensitive layer and, particularly, on the positively charging-type laminated photosensitive layer, it is made possible to obtain excellent electrically charging property and image-forming property while maintaining sufficiently great wear resistance and abrasion resistance.

Varistor-Type Surface Protecting Layer

According to the present invention, the aforementioned properties of the varistor-type surface protecting layer are obtained by adjusting in the dispersion system the blending ratio of the continuous phase of an electrically insulating resin and the dispersion phase of an electrically conducting fine powder dispersed therein and, at the same time, by adjusting the degree of dispersion of the two.

That is, as the blending ratio of the electrically conducting fine powder becomes greater than a predetermined range, the electrically conducting fine powder is dispersed in the form of chains or in cluster, whereby the electrically conducting agent dominates the electric properties causing the voltage-current characteristics to change linearly or causing the threshold electric field to decrease, which makes it difficult to obtain prop-

erties of the present invention. As the blending ratio of the electrically conducting fine powder becomes smaller than the predetermined range, on the other hand, the electrically insulating resin that exists among the electrically conducting fine particles dominates the electric properties, and the protecting layer becomes like an electrically insulating layer.

Contrary to the above-mentioned two cases, the nonlinear voltage-current characteristics of the surface protecting layer are accomplished by a dispersion system in which the effect of the interface between the electrically conducting fine particles and the electrically insulating resin is dominated by the light of electric characteristics, and hence there exist limitations in the blending ratio and dispersion condition of the two.

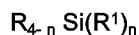
From the above-mentioned point of view, therefore, the electrically conducting fine powder should be present in an amount of from 10 to 40% by weight and, particularly, from 20 to 30% by weight in the whole covering layer though it may vary depending upon the kind thereof.

According to the study conducted by the present inventors by using an electron microscope, furthermore, it was found that in the dispersion system of the protecting layer that exhibits non-linear voltage-current characteristics, the electrically conducting fine particles do not exist in the aforementioned chain form or in cluster but exist in the form of independently dispersed particles, the average distance among the particles ranging from 100 to 500 Å.

Any resins can be used that are employed for the formation of a surface protecting layer of this kind. For instance, thermosetting resins such as a melamine-type resin, a urea-type resin and a silicon-type resin as well as thermoplastic resins such as a polyester resin, a polycarbonate resin, a fluorine-type resin and a polyarylate resin, can be used in a single kind or in a combination of two or more kinds. Desirably, the resin should impart excellent wettability and dispersibility to the electrically conducting powder.

The resin that is suited for forming a protecting layer having excellent toughness and wear resistance and that is suited for forming a varistor having non-linear voltage-current characteristics, can be represented by a highly crosslinked silicone resin, i.e., a thermosetting silicone resin.

The thermosetting silicone resin is formed by using in combination one or two or more silanes represented by the following general formula,



wherein R is a monovalent hydrocarbon group having up to four carbon atoms, R¹ is a monovalent group that can be hydrolyzed such as an alkoxy group with less than four carbon atoms or a halogen atom, and n is a number of from 1 to 4.

Examples of the monovalent hydrocarbon group R include alkyl groups such as a methyl group, an ethyl group and a propyl group; alkenyl groups such as a vinyl group and the like group; and aryl groups such as a phenyl group, a tolyl group and an ethylphenyl group. These silanes can be used in the form of a dimer, a trimer, a tetramer, or in the form of a linear or cyclic oligomer to form a silicone resin.

Suitable examples of the silanes include, though not limited thereto only, a monomethyltriethoxysilane, a dimethyldiethoxysilane, a trimethylethoxysilane, an ethyltrimethoxysilane, a phenyltriethoxysilane, a diphenyldimethoxysilane, a vinyltrimethoxysilane, an ethyl silicate, a dimethyl dichlorosilane, and the like. Among them, bi- to tetra-functional alkoxysilanes are preferred and, particularly, a tri-functional alkoxysilane is preferred.

The silicone resin used in the present invention may be comprised of a siloxane unit alone that is derived from the above-mentioned silane or an oligomer thereof, and may further be modified with a reforming resin such as a melamine resin, a benzoguanamine resin, an acrylic resin, or an epoxy resin.

The silicone resin used for the present invention should contain a silanol group (SiOH) in the molecules from the above-mentioned viewpoint of electric characteristics, the silanol group being contained at a concentration of electric characteristics, the silanol group being contained at a concentration of generally smaller than 30 millimoles per 100 g of the resin and, particularly, at a concentration of 1 to 10 millimoles per 100 g of the resin to fulfill the object of the present invention.

Any electrically conducting fine powder can be used that has heretofore been used for forming the low-resistance surface protecting layer of this kind. Desirably, the electrically conducting fine powder should have a volume resistivity of not greater than 10⁶ -cm as measured alone. Moreover, the grain size should be as fine as possible, and the average grain size should be smaller than 0.3 μm.

Suitable examples of the electrically conducting fine powder for forming the varistor-type surface protecting layer having non-linear voltage-current characteristics include a tin oxide-type electric conduction-imparting agent and, particularly, a tin oxide-type electric conduction-imparting agent doped with antimony oxide, phosphorus or fluorine. Particularly preferred example is an electric conduction-imparting agent which contains antimony oxide in an amount of 2 to 20% by weight with respect to the tin oxide.

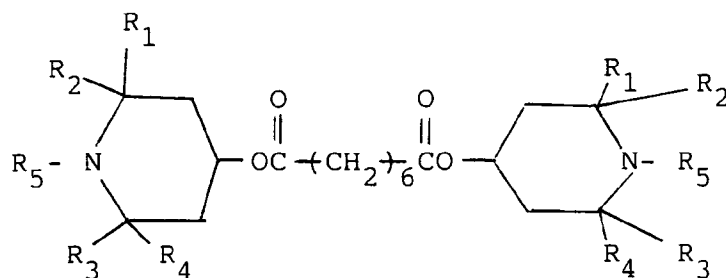
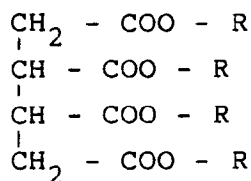
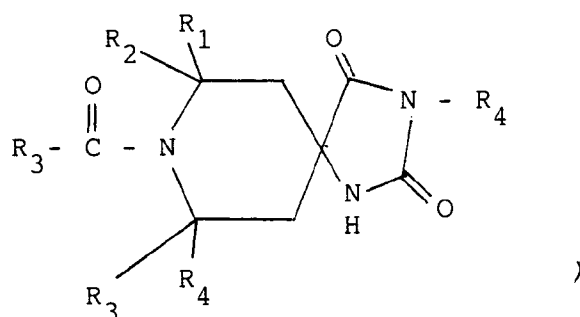
The electrically conducting fine powder and the resin should have excellent dispersibility mutually to each other, as well as excellent wettability, i.e., intimacy at the interface thereof, which seriously affect the electric

characteristics. In this sense, the electrically conducting fine powder should particularly desirably be treated with a silane-type coupling agent, a zirconium-type coupling agent, a titanate-type coupling agent, an aluminum-type coupling agent or a tin-type coupling agent that are known per se. The coupling agent should be used in an amount of 0.1 to 5 parts by weight per 100 parts by weight of the electrically conducting fine powder.

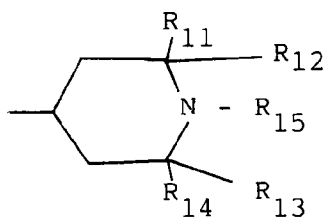
The thickness of the protective covering layer should usually range from 0.5 to 10 μm and, particularly, from 1 to 5 μm though it may vary depending upon the kind of resin.

The surface protecting layer is formed by preparing a solution or a dispersion of the above resin, and by applying it followed by drying and, as required, by effecting the baking. The solvent that is used should be the one that does not affect the photosensitive layer.

According to the present invention, the surface protecting layer may be blended with a blending agent which is known per se. For instance, antioxidizing agent such as hindered phenols, paraphenylene diamines, hydroquinones, organic sulfur compounds or organic phosphorus compounds can be contained in an amount of from 0.5 to 10 parts by weight per 100 parts by weight of the resin. Moreover, the hindered amines represented by the following general formula,



wherein R_1 to R_4 are alkyl groups having 1 to 4 carbon atoms, R_5 is a hydrogen atom or an alkyl group, R_1 is a hydrogen atom or an alkyl group, and R is a group represented by the following general formula,



wherein R_{11} to R_{14} are alkyl groups having 1 to 4 carbon atoms, and R_5 is a hydrogen atom or an alkyl group, can be contained as a photostabilizer in an amount of from 0.5 to 10 parts by weight per 100 parts by weight of the resin.

Photosensitive Material

The present invention can be adapted to a photosensitive material that has any organic photosensitive layer on an electrically conducting substrate. The photosensitive layer may consist of a single layer or a laminate of layers, and the present invention can be effectively adapted to a positively charging-type laminated photosensitive material which has an electric charge transporting layer (CTL) formed on the electrically conducting substrate and an electric charge generating layer formed thereon.

The positively charging-type laminated photosensitive layer is obtained by applying onto the electrically conducting substrate a coating solution that contains an electric charge transporting material, a binder resin and, as required, a solvent to form an electric charge transporting layer thereon and by applying on the electric charge transporting layer a coating solution which contains an electric charge generating material, a binder resin and, as required, a solvent to form an electric charge generating layer thereon.

Examples of the electric charge transporting material include fluorenone-type compounds such as a chloranil, a tetracyanoethylene, a 2,4,7-trinitrofluorenone and the like; nitrolyzed compounds such as a 2,4,8-trinitrothioxanthone, a dinitroanthracene and the like; hydrazone-type compounds such as an N,N-diethylaminobenzaldehyde, an N,N-diphenylhydrazone, an N-methyl-3-carbazolyl aldehyde, an N,N-diphenylhydrazone and the like; oxadiazole-type compounds such as a 2,5-di(4-dimethylaminophenyl)-1,3,4-oxadiazole and the like; styryl-type compounds such as a 9-(4-diethylaminostyryl)anthracene and the like; carbazole-type compounds such as an N-ethylcarbazole and the like; pyrazoline-type compounds such as a 1-phenyl-3-(p-dimethylaminophenyl)pyrazoline and the like; oxazole-type compounds such as a 2-(p-diethylaminophenyl)-4-(p-dimethylaminophenyl)-5-(2-chlorophenyl)oxazole and the like; isooxazole-type compounds; thiazole-type compounds such as a 2-(p-diethylaminostyryl)-6-diethylaminobenzothiazole and the like; amine derivatives such as a triphenylamine, a 4,4'-bis(N-(3-methylphenyl)-N-phenylamino) diphenyl and the like; nitrogen-containing cyclic compounds such as a stilbene-type compounds, a thiadiazole-type compound, an imidazole-type compound, a pyrazole-type compound, an indole-type compound, a triazole-type compound and like compounds; as well as a condensed polycyclic compound, anhydrous succinic acid, anhydrous maleic acid, dibromomaleic anhydride, a poly-N-vinylcarbazole, a polyvinylpyrene, a polyvinylanthracene, and an ethylcarbazole-formaldehyde resin. Here, the photoconducting polymer such as the poly-N-vinylcarbazole can also be used as a binder resin as will be described later. These electric charge transporting materials may be used in a single kind or in a combination of two or more kinds.

Moreover, examples of the electric charge generating may be a variety of widely known materials such as selenium, selen-tellurium, amorphous silicon, a pyrylium salt, an azo-type compound, a dis-azo-type compound, a tris-azo-type compound, an anthanthrone-type compound, a phthalocyanine-type compound, an indigo-type compound, a triphenylmethane-type compound, a type compound, a toluidine-type compound, a pyrazoline-type compound, a perylene-type compound and a quinacridone-type compound which can be used in a single kind or in a combination of two or more kinds.

Examples of the binder resin include a variety of photo-curable resin or polymers such as a styrene-type polymer, a styrene-butadiene copolymer, a styreneacrylonitrile copolymer, a styrene-maleic acid copolymer, an acrylic polymer, a styrene-acrylic copolymer, an ethylene-vinyl acetate copolymer, a polyester, an alkyd resin, a polyamide, a polyurethane, an epoxy resin, a polycarbonate, a polyacrylate, a polysulfone, a diallyl phthalate resin, a silicone resin, a ketone resin, a polyvinyl butyral resin, a polyether resin, a phenolic resin, as well as an epoxy acrylate and an urethane acrylate, which may be used in a single kind or in a combination of two or more kinds.

When the electric charge transporting layer is to be formed, the electric charge transporting material and

the binder resin should be mixed together at a suitable ratio. Usually, the binder resin is used in an amount of 30 to 500 parts by weight per 100 parts by weight of the electric charge transporting material. The electric charge transporting layer should be formed maintaining a suitable thickness which usually ranges from about 2 to 100 μm .

When the electric charge generating layer is to be formed, the binder resin may be used together. Or, the electric charge generating material may be formed directly on the electric charge transporting layer by vapor deposition, sputtering or the like method without using the binder resin.

When the electric charge generating layer is formed by using the binder resin, its amount usually ranges from 1 to 300 parts by weight per 100 parts by weight of the electric charge generating material. The electric charge generating layer should be formed maintaining a suitable thickness which usually ranges from about 0.01 to about 5 μm .

In preparing a coating solution for forming the electric charge generating layer and a coating solution for forming the electric charge transporting layer, any suitable organic solvent may be used, as required, depending upon the kinds of the resins contained in the layers to improve the coating property. The organic solvent may be suitably selected out of the aforementioned solvents used for the preparation of a coating solution for forming the protecting layer.

The photosensitive layer may contain a variety of additives such as terphenyl, halonaphthoquinones, acenaphthylenes, a widely used sensitizer, a plasticizer, an ultraviolet-ray-absorbing agent, and an antideterioration agent like an antioxidizing agent. Moreover, an intermediate layer may be formed between the electric charge generating layer and the electric charge transporting layer such that the electric charge smoothly migrates between the two layers. Even in preparing the coating solution for forming the electric charge generating layer and the coating solution for forming the electric charge transporting layer, there can be employed the aforementioned conventional mixing means and coating method that are used for preparing the coating solution for forming the protecting layer.

Examples of the electrically conducting substrate on which will be laminated the photosensitive layer consisting of the electric charge transporting layer and the electric charge generating layer include metals such as aluminum, an aluminum alloy, a steel, tin, platinum, gold, silver, vanadium, molybdenum, chromium, cadmium, titanium, nickel, palladium, indium, a stainless steel and a brass, as well as a glass substrate and a plastic substrate on which is formed a film of the above-mentioned metals oxides thereof by vapor deposition or the like method. The electrically conducting substrate may have the form of either a sheet or a drum.

The surface protecting layer (OCL) mentioned earlier is formed on the thus obtained photosensitive layer which consists of CTL and CGL.

Electrophotographic Method

According to the present invention, the above-mentioned photosensitive material is electrically charged under a condition where the electric field of the surface protecting layer is smaller than a threshold electric field thereof and is exposed to light to remove electricity under a condition where the electric field of the surface protecting layer is greater than the threshold electric field thereof.

First, the electric field of the surface protecting layer of the photosensitive material is controlled by a mechanism that is shown in Fig. 2. Here, the ratio $t_o/(t_o + t_p)$ should generally be set within a range of from 0.01 to 0.5 and, particularly, from 0.03 to 0.2.

The surface potential to the photosensitive material should be set to be 400 to 1500 V and, particularly, 600 to 1000 V in order to satisfy the above condition. The electric charging effected relying upon the corona charging of positive polarity.

Then, the electricity is removed by exposing the photosensitive material to the light of image. When the charging potential and the thickness ratio $t_o/(t_o + t_p)$ of the photosensitive layer to the surface protecting layer are set to lie within the above-mentioned ranges, the electric field applied to the surface protecting layer exceeds the threshold electric field E_{cr} when the photosensitive material is exposed to light and the electricity is effectively removed owing to the use of the varistor-type surface protecting layer having nonlinear voltage-current characteristics.

The exposure to light may be the slit exposure from the document or the scanning exposure using a laser beam, and the quantity of exposure should generally be from 2 lux.sec (0.6 $\mu\text{J}/\text{cm}^2$) to 10 lux.sec (3 $\mu\text{J}/\text{cm}^2$).

According to the electrophotographic method of the present invention, the image is formed by any widely known system except the above-mentioned point. For instance, the developing is effected relying upon a magnetic brush developing system using a two-component type magnetic developing agent or a one-component type magnetic developing agent, a noncontact type oscillation electric field developing system, or a developing system using a one-component type nonmagnetic developing agent. The toner image formed on the photo-

sensitive material can be fixed onto a copying paper or the like paper by a known method.

The invention will now be described by way of working examples.

(Example 1)

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100 Parts by weight of a 1,1-bis(p-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene, 50 parts by weight of a p-diethylaminobenzaldehydediphenyl hydrazone and 100 parts by weight of a polyarylate resin (U-100 produced by Unitika Co.) were dissolved in 900 parts by weight of dichloromethane. This solution was applied onto an aluminum cylinder pipe having an outer diameter of 78 mm and an inner diameter of 75 mm, and was dried at 100°C to form a carrier transporting layer. Here, the coating condition was so set that the film thickness was 25 µm after drying. Next, a dispersion solution was prepared by mixing and stirring 70 parts by weight of a dibromoanthanthrone, 30 parts by weight of an oxotitanium phthalocyanine, 50 parts by weight of a polyvinyl butyral (3000K produced by Denikagaku Kogyo Co.) and 3500 parts by weight of n-butyl alcohol, and was applied onto the above carrier transporting layer and was dried at 110°C to form a carrier generating layer. The coating condition was so set that the film thickness was 0.3 µm after drying.

Next, described below is a method of forming a varistor-type surface protecting layer which is an over-coating layer. First, 100 parts by weight of a methyltriethoxysilane and 1 part by weight of a hydrochloric acid solution of a concentration of 0.1 N are dissolved in 800 parts by weight of an ethyl alcohol, which was then refluxed for 30 minutes. The solvent of the solution of oligomer of the thus synthesized methyltriethoxysilane was substituted with an isopropyl alcohol, and then 5 parts by weight of an acrylic resin (BR-105 produced by Mitsubishi Rayon Co.) and 3 parts by weight of an antioxidizing agent (Tinubin 144 produced by Chiba Geigy Co.) were added to 100 parts by weight of the solid component thereof. Furthermore, 100 parts by weight of a tin oxide doped with antimony (10% by weight) and 0.5 parts by weight of a γ-glycidoxypropylmethyl-diethoxysilane were thrown into 200 parts by weight of an isopropyl alcohol, which was then refluxed for two hours. After cooled, the dispersion solution and the above-mentioned solution containing oligomer of the methyltriethoxysilane were mixed and stirred together. In this case, the mixing was so adjusted that the amount of the tin oxide doped with antimony was 40 parts by weight with respect to 100 parts by weight of the solid component of the methyltriethoxysilane oligomer. Then, the isopropyl alcohol was added in a suitable amount such that the solution viscosity was 4.5 cps. Finally, the solution was applied onto the carrier generating layer such that the film thickness was 2.2 µm after drying, and the heat treatment was effected under a condition of 120°C for 80 minutes in order to form the varistor-type surface protecting layer.

(Example 2)

8 Parts by weight of the dibromoanthanthrone, 120 parts by weight of the 1,1-bis(p-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene and 100 parts by weight of a bisphenol Z-type polycarbonate resin (Z-300 produced by Mitsubishi Gas Kagaku Co.) were dissolved in 900 parts by weight of a tetrahydrofurane. This solution was then applied onto an aluminum cylinder pipe having an outer diameter of 78 mm and an inner diameter of 75 mm and was dried at 100°C to form a carrier transporting layer. The coating condition was so set that the film thickness was 26 µm after drying. There was thus formed a single organic photosensitive layer of the positively charging type, and on which was then formed the varistor-type surface protecting layer which was quite the same as that of Example 1.

(Comparative Example 1)

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An organic photosensitive material similar to that of Example 1 was prepared in the same manner as in Example 1 but employing a simply electrically insulating surface protecting layer that did not contain antimonydoped tin oxide treated with γ-glycidoxypropylmethyldiethoxysilane.

(Comparative Example 2)

An organic photosensitive material similar to that of Example 1 was prepared in the same manner as in Example 1 but by using a so-called low resistance-type surface protecting layer by changing the amount of addition of the antimony-doped tin oxide treated with γ-glycidoxypropylmethyldiethoxysilane from 40 parts by weight into 100 parts by weight.

(Comparative Example 3)

5 An organic photosensitive material similar to that of Example 2 was prepared in the same manner as in Example 2 but by using a simply electrically insulating surface protecting layer that did not contain antimony-doped tin oxide treated with γ -glycidoxypropylmethyldiethoxysilane.

(Comparative Example 4)

10 An organic photosensitive material similar to that of Example 2 was prepared in the same manner as in Example 2 but using a so-called low resistance-type surface protecting layer by changing the amount of addition of the antimony-doped tin oxide treated with γ -glycidoxypropylmethyldiethoxysilane from 40 parts by weight into 100 parts by weight.

The thus prepared organic photosensitive materials of the positively charging type were evaluated for their electrostatic characteristics by using a common paper copying machine (DC-3285 produced by Mita Industrial Co., Ltd.) that is placed in the market. The exposure was carried out while changing the quantity of exposure on the surface of the photosensitive material over a range of from 0 to 6 lux.sec at a rate of 0.2 lux per a second. The attenuation of surface potential for the exposure was evaluated in terms of the potential at a developing portion (300 msec after the start of exposure). From the thus obtained relationship between the quantity of exposure and the potential at the exposed portion, the residual potentials as the exposed portion at the time of half exposure quantity and exposure quantity of 6 lux.sec were treated as sensitivity. The corona charging ability of the photosensitive material was evaluated in terms of the amount of the corona discharge current required for charging the surface potential to 800 V. Furthermore, the repetitive stability in the electrostatic characteristics was evaluated by repeating the electric charging and exposure to light to remove electricity 300 times while setting the initial dark portion charge potential to 650 V and the quantity of exposure to 3.5 lux.sec.

Table 1

	Charging ability ($\mu\text{A}/800\text{V}$)	Sensitivity		Repetitive stability	
		Half exposure quantity (lux.sec)	Residual potential at bright portion (V)	Charge in the charged potential at dark portion (%)	Charge in the residual potential at bright portion (%)
Example 1	322	2.0	75	-1.0	+0.2
Comparative Example 1	308	3.4	186	-17.4	-13.1
Comparative Example 2	charged only up to 275 V	—	—	—	—
Example 2	467	4.1	205	-3.2	+1.7
Comparative Example 3	413	5.9	313	-16.9	-24.8
Comparative Example 4	1349	4.2	203	-7.3	-13.6

In order to confirm the electrophysical value, furthermore, there were prepared a sample A having only the varistor-type surface protecting layer of Example 1 formed on an aluminum sheet (the surface protecting layer containing 27% by weight of a tin oxide doped with antimony (10% by weight), a sample B having only the resin component without antimony-doped (10% by weight) tin oxide, i.e., having an electrically insulating surface protecting layer formed on the aluminum sheet (corresponds to Comparative Example 1) (the surface protecting layer containing 0% by weight of the antimony-doped (10% by weight) tin oxide), and a sample C having a so-called low resistance-type surface protecting layer in which the amount of addition of the antimony-

doped (10% by weight) tin oxide treated with - glycidoxypropylmethyldiethoxysilane of Example 1 was changed from 40 parts by weight to 100 parts by weight (corresponds to Example 2) (the surface protecting layer containing 48% by weight of tin oxide doped with antimony (10% by weight). The film thickness were 2.1 μm (sample A), 1.8 μm (sample B) and 2.0 μm (sample C).

Then, the volume resistivities were measured at an electric field intensity of $1 \times 10^5 \text{ V/cm}$ by using a high resistivity measuring device (TR42 (sample measuring box), TR300C (DC stabilized power source), TR8652 (fine ammeter) produced by Advantest Co.). The volume resistivities were $6 \times 10^{15} \Omega\text{-cm}$ of the sample A, $3 \times 10^{17} \Omega\text{-cm}$ of the sample B, and $2 \times 10^{15} \Omega\text{-cm}$ of the sample C.

Furthermore, observation of cross sections of the sample A and the sample C using a transmission-type electron microscope revealed that fine particles of the antimony-doped (10% by weight) tin oxide were dispersed to maintaining a distance of about 200 to 500 $\text{\AA}$ in the sample A and that fine particles of the antimony-doped (10% by weight) tin oxide were locally coagulated in clusters or were locally continuous in chains in the sample C.

Claims

1. An electrophotographic method using a photosensitive material which has a photosensitive layer and a surface protecting layer formed on an electrically conducting substrate, in which the surface protecting layer is a varistor-type surface protecting layer having non-linear voltage-current characteristics, and the photosensitive material is electrically charged under a condition where an electric field of the surface protecting layer is smaller than a threshold electric field thereof and is exposed to light to remove electricity under a condition where the electric field of the surface protecting layer is greater than the threshold electric field thereof and is exposed to light to remove electricity under a condition where the electric field of the surface protecting layer is greater than the threshold electric field thereof.
2. An electrophotographic method according to claim 1, wherein the surface protecting layer has a threshold electric field of greater than $2 \times 10^5 \text{ V/cm}$ and a non-linear voltage coefficient of greater than 3.
3. An electrophotographic method according to claim 1 or claim 2 wherein the photosensitive layer is a photosensitive material consisting of a laminate of an electric charge transporting layer on the side towards the electrically conducting substrate and an electric charge generating layer on the side towards the surface protecting layer and is electrically charged to a positive polarity.
4. A surface-protected photosensitive material having a photosensitive layer and a surface protecting layer on an electrically conducting substrate, wherein the surface protecting layer is a varistor-type surface protecting layer having non-linear voltage-current characteristics.
5. A photosensitive material according to claim 4, wherein the surface protecting layer has a threshold electric field of greater than $2 \times 10^5 \text{ V/cm}$ and a non-linear voltage coefficient of greater than 3.
6. A photosensitive material according to claim 4 or claim 5 wherein the surface protecting layer consists of a resin composition which comprises a thermosetting resin or a thermoplastic resin and a fine electrically conducting powder dispersed in the resin in an amount of 10 to 40% by weight with respect to the whole amount, and has a volume resistivity of greater than $1 \times 10^{14} \Omega\text{-cm}$ as measured in an electric field of $1 \times 10^5 \text{ V/cm}$.
7. A photosensitive material according to any one of claims 4 to 6 wherein the thermosetting resin is a thermosetting silicone resin.
8. A photosensitive material according to any one of claims 4 to 7 wherein the electrically conducting fine powder is dispersed in the resin composition maintaining an average grain-to-grain distance of from 100 to 500 $\text{\AA}$ as measured by using an electron microscope.
9. A surface-protected photosensitive material of the positively charging type according to any one of claims 4 to 8 wherein the photosensitive layer consists of a laminate of an electric charge transporting layer on the side towards the electrically conducting substrate and an electric charge generating layer on the side towards the surface protecting layer.

- 10.** A photosensitive material according to claim 9, wherein the electrically conducting fine powder has an electron energy level which is higher by 0.05 to 1.00 eV than that of the electric charge generating substrate in the electric charge generating layer.

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FIG. 1

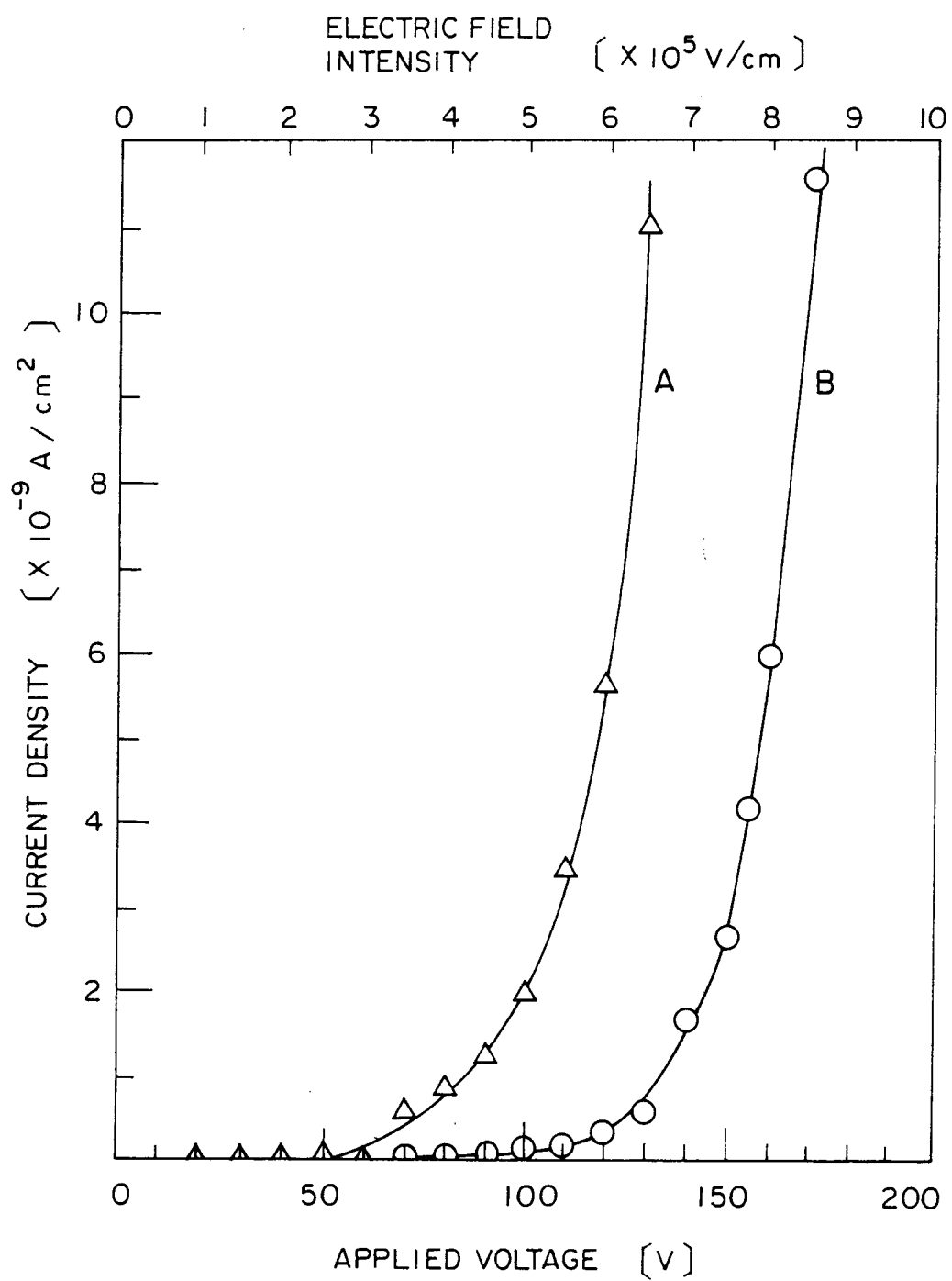


FIG. 2

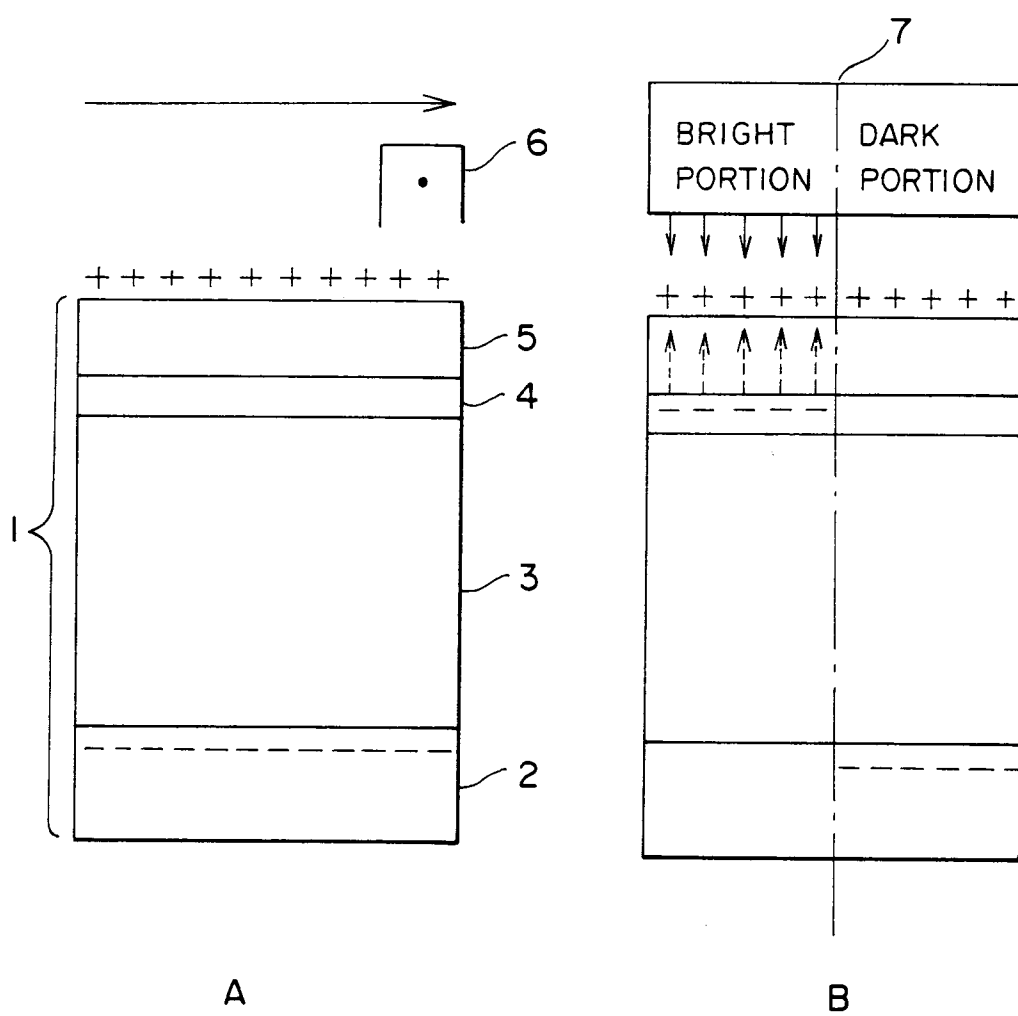


FIG. 3

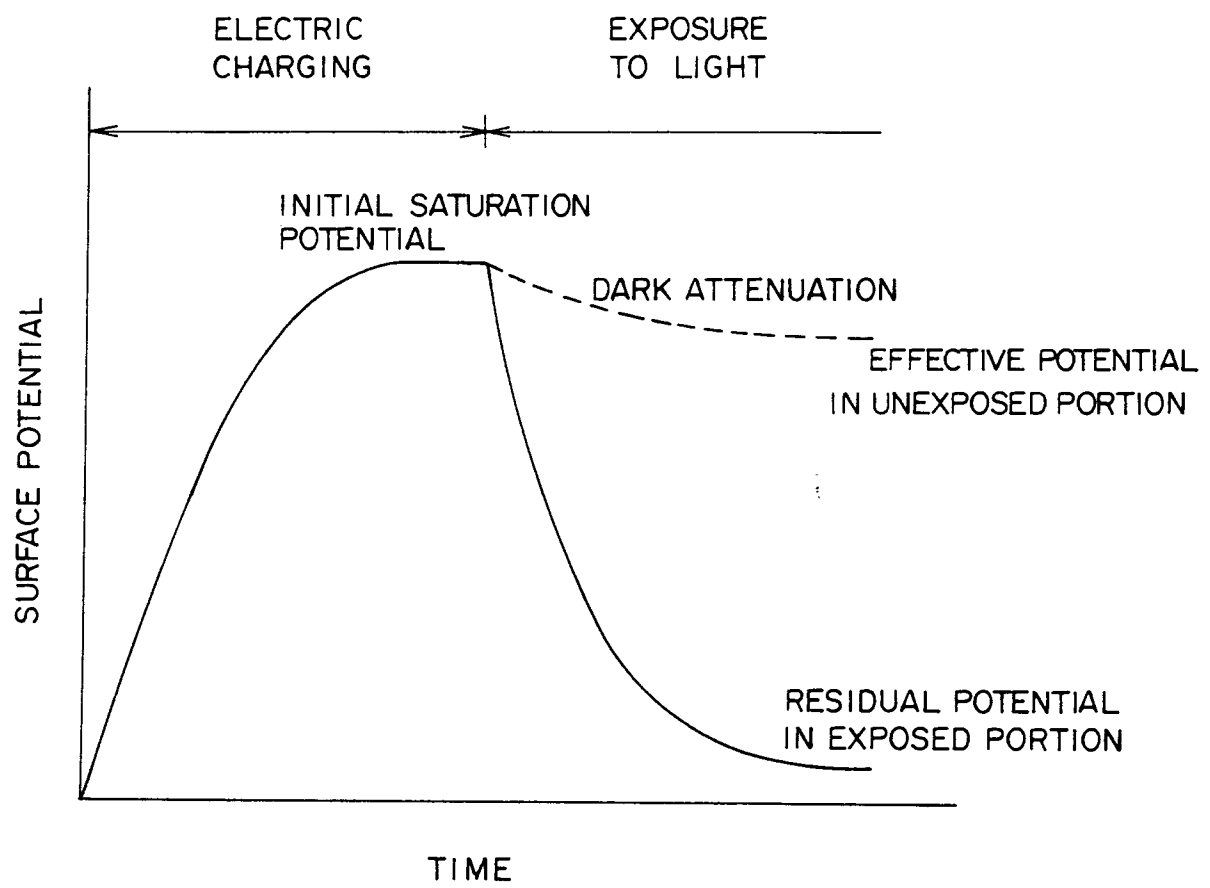
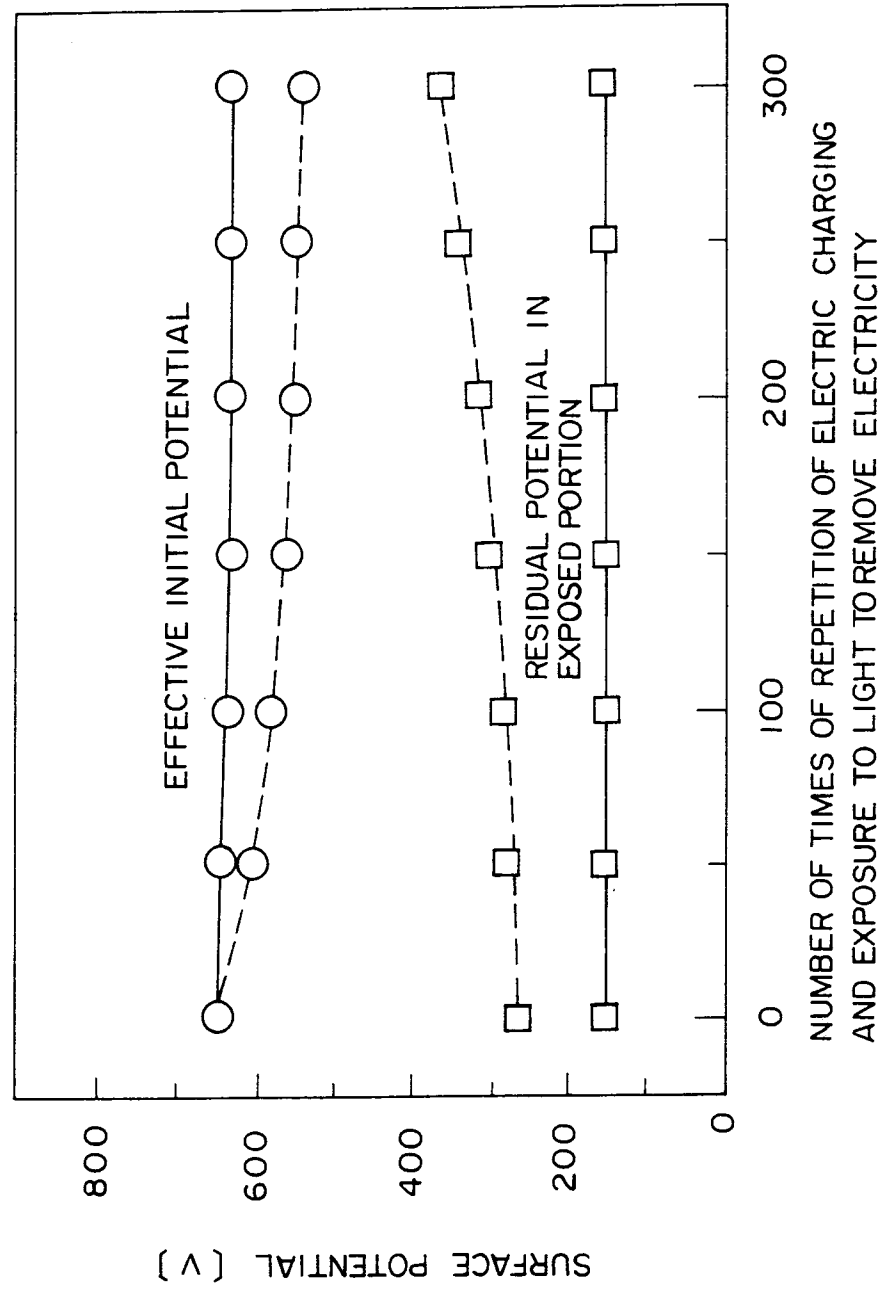


FIG. 4





European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 31 0645

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	DE-A-3 907 533 (SEIKOSHA) * column 2, line 8 - column 3, line 5; claims 1,2,4-6 *	1-5,9	G03G5/14 G03G5/147
A	EP-A-0 057 532 (XEROX) * page 4, line 1 - page 6, line 8; claims 1-6,8; examples I-IV *	6-8,10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27 JANUARY 1993	Examiner VANHECKE H.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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