In a photosensitive element comprising a transparent highly insulative layer, a photoconductive layer manifesting persistent internal polarization and an electrode layer which are bonded together into an integral unit, there is provided a series of low resistivity layers between the photoconductive layer and the electrode layer, the composition of the low resistivity layers being such that the resistivity thereof gradually approaches that of the photoconductive layer from the side thereof contiguous to the electrode layer.
PHOTOSENSITIVE ELEMENTS FOR USE IN ELECTROPHOTOGRAPHY

This is a division of application Ser. No. 147,927, filed May 28, 1971 now U.S. Pat. No. 3,795,515.

BACKGROUND OF THE INVENTION

This invention relates to a photosensitive element for use in electrophotography, more particularly to an improved photosensitive element including a photoconductive layer manifesting persistent internal polarization (PIP) effect.

In the method of electrophotography disclosed in U.S. Pat. Nos. 3,457,070 dated July 22, 1969 and 3,536,483 dated Oct. 27, 1970, use is made of a photosensitive element comprising a photoconductive layer manifesting persistent internal polarization and a transparent highly insulative layer integrally bonded to one side of the photoconductive layer. An electrostatic latent image is formed on the surface of the highly insulative layer by the steps of uniformly depositing a charge of a first polarity on the surface of the highly insulative layer thereby creating a uniform polarization charge in the photosensitive layer and then depositing a charge of the opposite polarity on the surface of the highly insulative layer concurrently with the projection of a light image on the photosensitive element.

The photosensitive element may include a second highly insulative layer on the opposite side of the photoconductive layer to improve the signal to noise ratio.

Advantageously, the first and second charges are deposited by the same or different corona discharge units.

The intensity of the latent image formed on the surface of the highly insulative layer per unit light input increases when the capacitance of the highly insulative layer is larger than that of the photoconductive layer. To this end it is desirable to decrease as much as possible the thickness of the highly insulative layer. Actually, however, it is extremely difficult to eliminate pin holes from the highly insulative layer and to form it to have a thickness of less than several microns from the standpoint of insulation strength. Thus, it is a practical requirement that the highly insulative layer have a thickness above a certain limit and it is the practice to design the highly insulative layer to have a thickness of more than 20 microns.

So long as the photosensitive element is made of a material of low light absorption, the resolution tends to decrease where an excessively thick photoconductive layer is used. Photoconductors of high photosensitivity generally have a high degree of light absorption so that it is desirable to use such materials from the standpoint of preserving high photosensitivity. We have investigated photosensitive elements in which it is possible to use materials capable of a high degree of light absorption, and can increase the thickness of the photoconductive layer so as to increase the efficiency of forming the latent image and thereby provide high resolution. When a thick photoconductive layer of high light absorption is subjected to light excitation from only one side thereof as in conventional electrophotography, some portions will not be excited by light. For example, where SeTe or Se is used, nearly all light that causes efficient light excitation is absorbed within a thickness of the photoconductive material of less than 1 micron. Accordingly, where the SeTe layer has a thickness of 20 microns most of it will not be excited by the light and the percentage of the thickness subjected to light excitation decreases with the thickness of the photoconductive layer. Notwithstanding the high degree of light absorption, thick layers of SeTe or Se are now used in photosensitive elements for electrophotography because the mobility of free charge carriers in the semiconductor body under an electric field is very high. The mobility amounts to 0.14 cm²/V·sec. in Se which is regarded as having the lowest mobility. This means that even a Se layer having a thickness of more than several tens of microns can be used for electrophotography with satisfactory results.

The same situation prevails in the above described method of electrophotography so that this method also can employ materials of extremely high light absorption such as Se, SeTe, CdTe, etc.

However, high speed cyclic operation with a photosensitive element including a thick photoconductive layer of the type to above results in a type of fatigue or hysteresis due to residual charge which causes a decrease in the latent-image-forming ability of the photosensitive element.

It was found that such fatigue is particularly significant in a photosensitive element having highly insulative layers on both sides of the photoconductive layer, and that such fatigue is generally of the same type as that experienced in conventional Xerography.

SUMMARY OF THE INVENTION

It is an object of this invention to provide a new and improved photosensitive element for use in electrophotography which can eliminate the effect of residual charge.

Another object of this invention is to provide an improved method of manufacturing a photosensitive element which can be used many times without suffering from the adverse effects of residual charge or hysteresis.

According to this invention, in a photosensitive element of the class comprising a transparent highly insulative layer, a photoconductive layer manifesting persistent internal polarization and an electrode layer which are laminated in the order mentioned and are bonded together into an integral unit, there is provided a series of low resistivity layers between the photoconductive layer and the electrode layer, the resistivity of the low resistance layers gradually approaching that of the photoconductive layer from the side thereof contiguous to the electrode layer. Preferably, the amount of photoconductive material manifesting persistent internal polarization in the low resistivity layers gradually decreases from the side thereof contiguous to the photoconductive layer as if the photoconductive material were diffused in the low resistivity layers so that there is no discrete interface between the photoconductive layer and the low resistivity layers. For this reason, such a series of low resistivity layers is hereinafter often called a "diffused layer." Such a series of low resistivity layers can be prepared by first forming a layer of low resistivity material on the surface of an electrode layer, then a layer containing both the low resistivity material and the photoconductive material and finally a layer containing the photoconductive material alone, by vapor deposition or spray coating or a like technique.

By increasing the number of intermediate layers containing varying proportions of low resistivity material and photoconductive material manifesting persistent
internal polarization or photoconductive PIP material, the composition of the respective layers varies gradually which is desirable to eliminate discrete interfaces between layer.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawing:

FIG. 1a to FIG. 1c show diagrams which explain charge distributions in a photosensitive element utilizing photoconductive PIP material when a latent image is formed by the method described above;

FIG. 2 is a view similar to FIG. 1 but the photoconductive layer and the electrode layer are not in perfect ohmic contact;

FIGS. 3 and 4 show two examples of photosensitive elements embodying the invention; and

FIG. 5 is a diagram showing a vacuum vapor deposition apparatus suitable for preparing the photosensitive element of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The photosensitive element shown in FIGS. 1a, 1b and 1c and used to form a latent image in the method of electrophotography described above comprises a transparent highly insulative layer 1, a photoconductive layer 2 and an electrode layer 3 which are laminated in the order mentioned and bonded together into a unitary structure. It is assumed herein that the photoconductive layer 2 is a material of p-type conductivity and contains a plurality of charge trapping levels, such as SeTe. FIG. 1a shows the charge distribution in the element after a negative charge is uniformly deposited on the surface of the highly insulative layer 1. A negative charge is present and forms an internal polarization as shown in FIG. 1a. Since it is assumed that the photoconductor has p-type conductivity, the majority carriers thereof are positive and the negative charge carriers migrate very little. Thus, in the free state the majority carriers are caused to migrate through the photoconductive layer by the attraction of the negative charge deposited on the highly insulative layer, but such migration of the majority carriers is blocked by the highly insulative layer and the carriers are trapped in the photoconductive layer near the interface between it and the highly insulative layer. The symbol @ represents such trapped charge.

In the second step, positive charge is deposited on the surface of the highly insulative layer 1 concurrently with the projection of a light image upon the photoconductive layer 2 through the highly insulative layer 1. The left-hand half of FIG. 1b shows the portions corresponding to bright portions of the light image while the right-hand half corresponds to dark portions of the light image. At bright portions, under the influence of the positive charge newly deposited on the highly insulative layer the positive charge carriers migrate through the photoconductive layer thus creating a charge distribution as shown on the lefthand half of FIG. 1b. On the other hand, at dark portions of the light image since there is no migration of charge in the photoconductive layer the charge that has been trapped in the photoconductive layer near the interface remains unchanged. Since the deposition of charge during the second step is made so that the surface potential of the highly insulative layer becomes uniform whether a corona discharge unit or an electrode urged against the surface of the highly insulative layer is used, deposition of the positive charge upon the highly insulative layer is restrained at the dark portions of the light image. A charge distribution is thus created as shown in the righthand portion of FIG. 1b having a density of positive charge which is different from that at the bright portions of the light image shown on the lefthand half. The trapped charge @ is excited again when the latent image is irradiated with uniform light, for example, light emanating from an electric lamp or daylight, or after elapse of a suitable time interval to create new free charge carriers. This changes the charge distribution at portions corresponding to dark portions of the light image to that shown in FIG. 1c. Since the latent image formed in the second step and having different densities of positive charge at various portions corresponding to the light image creates an external effect as a potential image, the image can be developed to form a visible image by any suitable method of development, for example by using a charged toner. Thereafter, the developed powder image can be transferred printed onto a recording medium such as paper. Then the photosensitive element is restored to the original state for the next cycle by any known method of cleaning including erasure of the residual latent image and removal of the remaining toner.

Unless the photoconductive layer and the electrode layer are in perfect ohmic contact, some of the charge carriers that migrate towards the electrode layer during the second step and the succeeding step are trapped in the portion of the photoconductive layer near the electrode layer as shown in FIG. 2. Such trapped charge cannot be released because of the strong light absorption property of the photoconductive material as described above. For this reason, such trapped or residual charge causes hysteresis and the perfect charge separation shown in FIG. 1a cannot be expected in the succeeding cycles of operation. The effect of hysteresis is cumulative with the number of cycles, thus limiting the useful life of the photosensitive element. It should be noted that where a second highly insulative layer is interposed between the photoconductive layer and the electrode layer the effect of hysteresis is particularly significant due to the current blocking action of the second highly insulative layer.

We have now succeeded in eliminating the adverse effects of hysteresis by providing a low resistivity layer between the electrode layer and the photoconductive PIP layer as described above.

More particularly, as shown in FIG. 4, the bottom portion or low resistivity layer 2a of the photoconductive layer 2 contiguous to the electrode layer 3 is constructed as if it were diffused with photoconductive PIP material or a similar substance so that there is no discrete interface between layer 2a and the bulk of the photoconductive PIP layer 2. In a modified photosensitive element a second highly insulative layer 1a is interposed between the diffused layer 2a and the electrode layer 3. In the conventional photosensitive element wherein the photoconductive layer is firmly bonded to the electrode layer or conductive substrate, due to the difference in the work functions of these two materials it is difficult to form perfect ohmic contact thereof between so that a certain degree of current blocking action occurs at the interface causing undesirable hysteresis, as has been set forth hereinabove.
However, provision of the low resistivity layer 2a which manifests the property of metal and does not, or only to a slight extent, trap charge carriers, for instance a layer of a SeTe alloy containing a large proportion of Te, avoids interference with migration of the charge carriers. Thus, the charge carriers migrating towards the electrode layer can easily reach the low resistivity layer and are stored therein as free charges so that trapping of the charge carriers described in connection with FIG. 2 can be eliminated. Since the trapping of charge carriers in the region of the photoconductive layer adjacent the electrode layer is thus substantially precluded, there is no chance of residual charge giving rise to hysteresis. For this reason, the novel photosensitive element can be used many times at high speed.

The electrode layer is not limited to being metal but may be any material having relatively low resistivity such as a thin foil of metal, conductive paper or conductive glass. Further, the composition of the photoconductive layer and the low resistivity layer is not limited to the particular materials illustrated and many other combinations may be used. For example, in the case of a SeTe photoconductive layer, alloys containing varied quantities of Se and Te are prepared. At first pure Te or an alloy of Te and Se containing only a small quantity of Se is vapor deposited on the surface of an electrode layer. The film thus formed consists of Te only or an alloy of SeTe containing only a small quantity of Te and acts as a low resistance layer. Then mixtures or alloys of Te and Se with decreasing proportions of Te are sequentially vapor deposited on the Te layer. Finally, a layer containing Se alone or an alloy of SeTe containing a small quantity of Te is vapor deposited to form the bulk of the photoconductive layer. In this manner, a layer with gradually varying content of the photoconductive PbTe material is provided between the electrode layer and the bulk of the photoconductive layer. Especially the Te layer or Te rich layer contiguous to the electrode layer eliminates imperfect ohmic contact to the electrode layer thus preventing trapping of charge carriers.

In the modified photosensitive element shown in FIG. 4 including highly insulative layers or current blocking layers 1 and 1a on both sides of photoconductive layer 2, low resistivity layer 2a perfectly prevents the flow of charge carriers between the photoconductive layer 2 and the electrode layer 3 and the current rectifying properties and current blocking properties between these layers do not cause any adverse effects. The function of the second highly insulative layer can also be obtained by using a metal electrode having an oxide coating.

The low resistivity layer can be advantageously formed by vacuum deposition techniques. Especially in the case of selenium alloys, vacuum deposition of the bulk of the photoconductive layer and the low resistivity layer can be readily accomplished by using a number of boats containing different raw materials. Where the low resistivity layer similar to a diffused layer and the bulk of the photoconductive layer are made by using a powder of photoconductive material dispersed in an electric insulative binder two or more mixtures of powders of the binder and photoconductive material are prepared and are sequentially coated on an electrode layer in such a manner that the amount of material that does not manifest charge trapping characteristics or has less tendency to trapping charge increases toward the electrode layer. In this type of photosensitive element, since the composition of the photoconductive layer does not vary gradually the characteristics of the photosensitive element are not as good as those of the element prepared by vacuum deposition but are much better than those of the prior art element shown in FIG. 1.

To impart a better understanding of the invention the following examples are given.

EXAMPLE 1

Vapor deposition apparatus schematically shown in FIG. 5 was used comprising flash vapor deposition sources 12 and 13 and a conventional vapor deposition source 14. Hopper 15 was filled with a powder of SeTe alloy containing 16 mol % of Te which serves as a photosensitive material having a large number of trap levels. Hopper 16 was filled with a powder of SeTe alloy containing 40 mol % of Te which serves as a high sensitivity photoconductive material or material having a small number of charge trapping levels. Boat 14 was filled with a powder of pure Te. A thin aluminum substrate 17 having a thickness of 1 mm and coated with a film of a polycarbonate resin having a thickness of 2 to 4 microns was placed in the upper portion of the vapor deposition tank 18. A shutter 19 was located beneath the aluminum substrate 17. After the tank 18 had been evacuated boat 14 was heated to vapor deposit Te upon the polycarbonate film on aluminum substrate 17. When the thickness of the Te layer deposited on the aluminum substrate had reached 3 microns the temperature of boat 12 was raised to 400° to 500°C and the powder of SeTe alloy containing 16 mol % of Te was supplied from hopper 15 to boat 12 whereby to deposit a layer containing both the SeTe alloy and Te on the Te layer. Deposition of Te was continued until the thickness of the deposited layer reached 5 microns and thereafter the deposition of the SeTe alloy alone was continued until the thickness of the SeTe layer reached 50 microns. Then the temperature of boat 13 was raised to 500° to 600°C and the powder of SeTe alloy containing 40 mol % of Te was supplied to boat 13 from hopper 16 to deposit this SeTe alloy together with the SeTe alloy containing 16 mol % of Te. When the thickness of the deposited layer containing both SeTe alloys reached about 1 micron, the deposition operation was ceased and the coated aluminum substrate 17 was removed from the vapor deposition tank 18. A transparent highly insulative layer of polycarbonate resin was then applied on the SeTe alloy layer to a thickness of 10 microns thus providing a photosensitive element having the construction shown in FIG. 4. As can be seen from FIG. 3, the first polycarbonate layer on the aluminum substrate may be omitted.

EXAMPLE 2

A fine powder of CdS:Cu photoconductive material having a mean particle size of 3 microns was prepared by firing CdS containing 10⁻⁴ mol % of copper as the activator and chlorine as the coactivator at a temperature of 600°C for about 1 hour. Then 10⁻⁴ mol % of copper and a small quantity of S were added to this CdS powder and the mixture was fired again at a temperature of 600°C for 15 minutes in N₂ atmosphere without incorporating a coactivator to obtain a CdS:Cu powder having a large number of trapping levels. Further, another fine powder of CdS:Cu photoconductive material
having a mean particle size of 3 microns was prepared by firing CdS containing 10⁻⁷ mol % of copper as the activator and chlorine as the coactivator at a temperature of 600°C for about 1 hour. The last material is not generally considered to be an excellent photoconductive material because of its low dark resistance but is characterized in that it can readily exchange charge carriers with other materials. Each of the CdS:Cu powders was dispersed in an organic solvent containing 7 % by weight of vinyl acetate. At first a solution of the CdS:Cu powder activated with 10⁻⁶ mol % of copper was sprayed on an aluminum substrate. Then both solutions were sprayed concurrently. The nozzle of the spray gun spraying the solution of the CdS:Cu activated with 10⁻⁶ mol % of copper was gradually throttled and then only the solution of the CdS:Cu activated with 10⁻⁵ mol % of copper was applied. The total thickness of the photoconductive layer was 80 microns, the thickness of the upper layer which manifests strong charge trapping or persisting internal polarization properties and of the bottom layer of low resistance being about 10 microns each.

A highly insulating layer was applied on the top of the photoconductive layer to complete a photosensitive element. As is well known in the art it is possible to activate CdS with materials other than copper, for example gold, silver, manganese and the like. The firing temperature and firing time of course vary depending upon the photoconductive material and activator. It was found that the photosensitive elements of both examples could be used repeatedly in the method of electrophotography described above without the accompanying effect of hysteresis. It is to be understood that any well known photosensitive photoconductive materials manifesting persistent internal polarization can be used in this invention. Among photoconductive materials manifesting persistent internal polarization or which can readily be imparted with this property are CdS, CdSe, Se, SeTe, ZnSe, ZnS, [ZnCd]₅Sn, ZnO, PbO, metal sulfides, metal oxides, intermetallic compounds, anthracene, anthraquinone, and other organic compounds. The low resistivity layer may be formed of low resistance materials prepared by modifying the above described photoconductive PIP materials by incorporating other substances or activators, or may be formed of low resistivity materials which do not manifest internal persistent polarization and do not trap charge carriers. Strictly speaking, it is advantageous to use a low resistivity material which is a semiconductor and whose majority carriers have the same polarity as those of the PIP material. However, if the mobility of the minority carriers of the PIP material is sufficiently low, the condition just described is not essential. Further, any transparent highly insulating material may be used for the highly insulating layer such as polyester, epoxide, polyethylene, polyurethane and poly carbonate.}

We claim:

1. A method of manufacturing a photosensitive element for use in electrophotography by the steps of disposing a first source of a first photoconductive material exhibiting persistent internal polarization properties, a second source of a second such material having lower resistivity than said first material and an electrode layer in a vapor deposition tank, operating said second source to deposit said second material on said electrode layer, concurrently operating said first and second sources to deposit a mixture of said first and second materials, operating said first source to deposit said first material alone to a thickness greater than the combined thickness of said second material and said concurrently deposited first and second materials, and applying a highly insulative layer upon the deposited layer of said first material.

2. The method according to claim 1 which further utilizes a third source of metal and wherein said third source is first operated before said second source to deposit a layer of said metal between said electrode layer and the deposited layer of said second material.

3. The method according to claim 1 wherein said electrode layer is provided with a highly insulative layer and said second material and said mixture of said first and second materials are sequentially deposited upon said highly insulative layer.

4. The method according to claim 1 wherein said first material comprises a SeTe alloy containing 16 mol % of Te and said second material comprises a SeTe alloy containing 40 mol % of Te.

5. The method according to claim 2 wherein said third source comprises Te.

6. A method of preparing a photosensitive element for use in electrophotography comprising the steps of providing a conductive base as an electrode layer, preparing a first organic solution of photoconductive material exhibiting persistent internal polarization properties and a second organic solution of such material having lower resistivity than said photoconductive material of said first solution, applying said second organic solution upon said electrode layer to form a layer of said lower resistivity material, concurrently applying said first and second organic solutions to form a layer of a mixture of said photoconductive material exhibiting persistent internal polarization properties and said lower resistivity material, applying said first organic solution to form a layer of said photoconductive material exhibiting persistent internal polarization properties and applying a transparent insulating layer upon the last mentioned layer.

7. A method of manufacturing a photosensitive element for use in electrophotography comprising the steps of providing a conductive base as an electrode layer, forming on said electrode layer a low resistivity layer which includes photoconductive materials, forming a photoconductive layer on said low resistivity layer, and applying a transparent highly insulative layer on said photoconductive layer, said low resistivity layer being formed to a thickness less than that of said photoconductive layer and being formed by depositing a series of interdiffused layers of varying resistivity such that the resistivity thereof is a minimum adjacent said electrode layer and increases toward said photoconductive layer to a value approaching that of said photoconductive layer, thereby eliminating any discrete interface between said photoconductive layer and said low resistivity layer.

8. The method as claimed in claim 7 wherein said series of inter-diffused layers includes a layer of pure metal in contact with said electrode layer and a second layer including said metal and a photoconductive material exhibiting persistent internal polarization properties.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,894,870
DATED : July 15, 1975
INVENTOR(S) : Koichi Kinoshita and Tadaji Fukuda

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

On the title page, reference should be made to the corresponding Japanese application Serial No. 45787/70, filed May 29, 1970, from which priority is claimed.

Column 2, line 19 after "layer of the type" insert --referred--.

Column 2, line 47 change "resistance" to --resistivity--.

Signed and Sealed this
twenty-eight Day of October 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks