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Tanaka et al.

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[45] **May 6, 1975**

[54] **ELECTROPHOTOGRAPHIC SENSITIVE PLATE**

[75] Inventors: **Susumu Tanaka; Katsutoshi Konishi,** both of Osaka, Japan

[73] Assignee: **Minolta Camera Kabushiki Kaisha,** Osaka-shi, Japan

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[21] Appl. No.: **369,134**

Related U.S. Application Data

[63] Continuation of Ser. No. 152,569, June 14, 1971, abandoned.

[30] **Foreign Application Priority Data**

June 15, 1970 Japan 45-51335

[52] **U.S. Cl.** ..... **96/1.5; 96/1 SD**

[51] **Int. Cl.** **G03g 5/02**

[58] **Field of Search** 96/1.5-1.8; 252/501; 117/215, 201, 218

[56] **References Cited**

UNITED STATES PATENTS

2,745,237	5/1956	Mengali	96/1.5
2,901,348	8/1959	Dessaner et al.	96/1.5
3,170,790	2/1965	Clark	96/1.5
3,598,582	8/1971	Herrick et al.	96/1.5

Primary Examiner—Norman G. Torchin
Assistant Examiner—John L. Goodrow
Attorney, Agent, or Firm—Watson, Cole, Grindle & Watson

[57] **ABSTRACT**

An electrophotographic sensitive plate is formed by depositing first and second photoconductive layers on a conductive substrate in which the first photoconductive layer provides a rectifying barrier for preventing the injection of charges from the substrate and the second photoconductive layer is formed in a reticulated pattern. The second photoconductive layer may comprise a mixture of selenium with an element selected from the group consisting of Te, As and Sb. One of the photoconductive layers has a greater sensitivity than the other so as to improve the fidelity of half tone image reproduction. A transparent organic semiconductor layer is formed on the second photoconductive layer to maintain electric charges on its surface and for transporting photo-charge carriers generated within the first and second photoconductive layers. In an alternative embodiment the second photoconductive layer comprises a mixture in which the amount of the selected element is less than the amount of the selected element in the first photoconductive layer.

5 Claims, 11 Drawing Figures

FIG. 1(A)

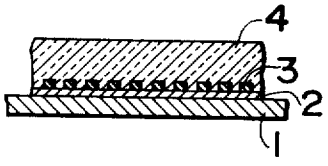


FIG. 1(B)

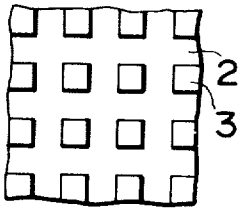


FIG. 2(A)

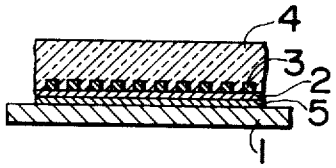


FIG. 2(B)

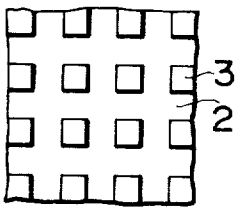


FIG. 3(A)

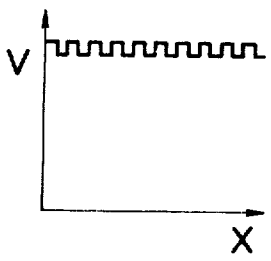


FIG. 3(B)

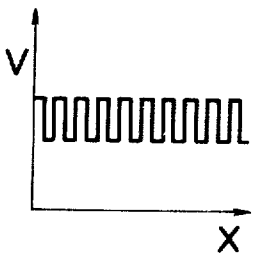
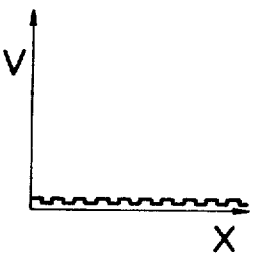


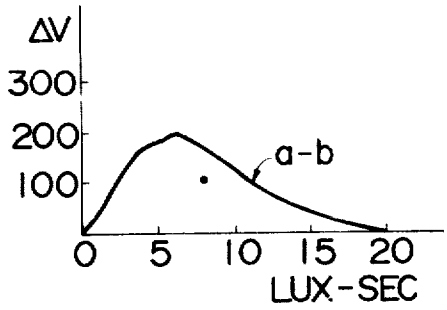
FIG. 3(C)



INVENTOR.
SUSUMU TANAKA
KATSUTOSHI KONISHI
BY
WATSON COLE GRINDLE & WATSON

ATTORNEYS

FIG. 4(B)



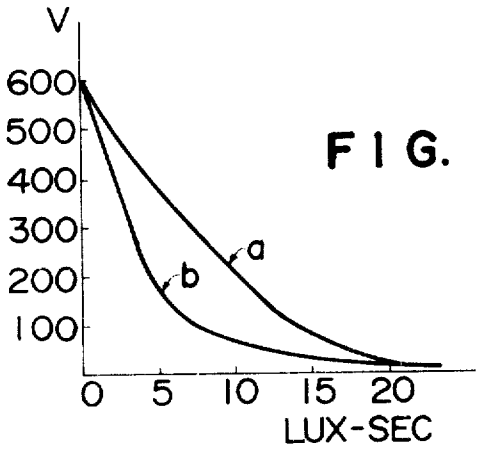


FIG. 4(A)

FIG. 5(A)

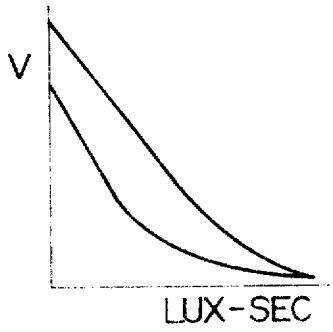
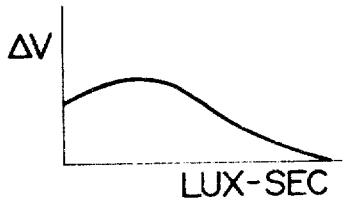


FIG. 5(B)



INVENTOR.
SUSUMU TANAKA
KATSUTOSHI KONISHI
BY
WATSON COLE GRINDLE & WATSON
ATTORNEYS

ELECTROPHOTOGRAPHIC SENSITIVE PLATE

This is a Continuation application Ser. No. 152,569 filed June 14, 1971.

BACKGROUND OF THE INVENTION

The present invention relates to an electrophtographic sensitive plate, and more particularly to such a plate which is capable of recopying an original picture by reproducing the half tones thereof with fidelity.

For the purpose of improving the conventional electrophotographic sensitive plate which has characteristics not capable of reproducing half-tones, the methods using an optical method which uses a mesh screen such as in photomechanical processes or an electrical method which hold the meshwork resolving function of an image electrically on the surface of an electrophotographic sensitive plate have been proposed.

However, the former method is defective in that it tends to lower the contrast of the picture image owing to its meshed screen, and the latter method in which a selenium layer vacuum evaporated on a conductive base plate is formed as a pattern by means of, for example, notching therein is defective in that the photosensitive plate lacks smoothness so as to lose its durability, as well as its sensitivity is lowered. In order to improve these defects another photosensitive plate has been used which is provided with another layer between the conductive base plate and the photoconductor layer in order to prevent electric charges from coming into the photoconductor layer from the conductive base plate, and of which the rectifying property is formed by another reticulated layer. This photosensitive plate in that the has an advantage smoothness of the surface of the photosensitive plate is not lost, but is still defective in that the lowering of its sensitivity and contrast cannot be avoided because of the sensitivity depending entirely upon the photoconductor layer and the rectifying property being obtained by the layer reticulated.

In a copending application Ser. No. 151,713, filed June 10, 1971, the inventors have disclosed an electrophotographic sensitive plate which is composed of three layers comprising a high resistant photosemiconductor layer which is closely in contact with and covers a conductive base plate and which forms a high rectifying barrier capable of preventing electric charges from migrating thereinto from the conductive base plate. A thin layer is coated thereon and composed of a low resistant and highly sensitive panchromatic photoconductive substance which generates optical charge carriers due to light rays absorbed by the overall thin layer. A transparent high resistant semiconductor layer which is further coated thereon and which functions as an electric charge holder as well as a means for the passage of the generated photo-charge carriers.

The high resistant photo-semiconductor of this photosensitive plate is composed of a low sensitive photoconductive substance with an extremely low sensitivity and is endowed with a rectifying barrier as described above. While the low resistant photoconductor layer which generates electric charge carriers is composed of a high sensitive photoconductive substance, and its sensitivity and panchromativity are far superior to the photoconductor layer of the prior Carlson type.

The present invention makes use of the photosensitive plate disclosed by that invention and to apply it to an electrophotographic sensitive plate which is capable of reproducing good half tones.

OBJECTS OF THE INVENTION

One object of the present invention is to provide an electrophotographic sensitive plate which is capable of reproducing good half tones.

Another object of this invention is to provide an electrophotographic sensitive plate with a high sensitivity and good panchromativity, which is therefore capable of reproducing good half tones.

A further object of this invention is to provide an electrophotographic sensitive plate which is capable of reproducing a linear picture with a high contrast, as well as reproducing good half tones.

Further another object of this invention is to provide an electrophotographic sensitive plate which is smooth, has good durability, is sensitive and capable of reproducing good half tones.

SUMMARY OF THE INVENTION

The present invention provides an electrophotographic sensitive plate composed of laminated layers comprising a semiconductor layer uniformly deposited on a conductive base plate, two photoconductor layers which are sequentially formed on the semiconductor layer, and each of which have different sensitivities due to one photoconductor layer being composed of a high resistant photoconductive substance while the other photoconductor layer is composed of a low resistant and highly sensitive photoconductive substance. The one photoconductor layer is formed as a uniform layer, whereas the other photoconductor layer is reticulated. A transparent organic semiconductor layer is also laminated onto one of the photoconductor layers, wherein the uniform semiconductor layer on the conductive base plate is endowed at its contacting surface therewith with a high rectifying barrier characteristic to preventing electric charges from migrating into the photoconductor layer from the conductive base plate. The photoconductor layer with low resistance and with high sensitivity is endowed with the characteristic of generating photo-charge carriers by primarily absoring light rays, as well as in cooperation with the other photoconductor layer which has been reticulated, endowed with a meshwork resolving function. Further, the transparent organic semiconductor layer is endowed with characteristic of an electric charge holder and as a means for the passage of photo-charge carriers which are generated in the photoconductor layers. Thus all the functions which are partially taken charge of by the individual layers are accumulated so that the electrophotographic sensitive plate displays its advantageous ability to reproduce good half tones.

Furthermore, in an electrophotographic sensitive plate construction as set forth above, in order to obtain a high resistant photoconductor layer, such a photoconductive substance is selected that is capable of forming a high rectifying barrier by keeping contact with the conductive base plate. Thereby, the functional achievement of the semiconductor layer is also substituted by that layer, these two layers can be coordinated into one layer, thereby it becomes possible to obtain an electrophotographic sensitive plate which is highly sensitive and able reproduce repreoduce good half tones accordingly.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A and 1B show an embodiment of an electronic photograph photosensitive plate in accordance with the present invention, wherein FIG. 1A is an elevational section view thereof, and FIG. 1B is an enlarged partial plan view thereof.

FIGS. 2A and 2B show another embodiment wherein FIG. 2A is an elevational section view thereof, and FIG. 2B is an enlarged partial plan view thereof.

FIGS. 3A–3C show the potential distribution of an electronic photograph photosensitive plate in accordance with this invention, wherein FIG. 3A shows the potential distribution for the light part of a picture image, and FIG. 3B is the potential distribution for the half tone part, and FIG. 3C is the potential distribution for the dark part of a picture image.

FIGS. 4A and 4B show the light decay characteristics of an electronic photograph photosensitive plate in accordance with this invention, wherein FIG. 4A is the light decay characteristics at two points of the identical photosensitive plate where the properties thereof are different from each another, and FIG. 4B shows the potential distribution characteristics due to the difference therebetween.

FIGS. 5A and 5B show the light decay characteristics of another photosensitive plate in accordance with this invention, wherein FIG. 5A is the light decay characteristics at two points of the photosensitive plate where the properties thereof are different from each other, and FIG. 5B shows the potential distribution characteristics due to the difference therebetween.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Describing in detail the constitution of the present invention with reference to drawings, reference numeral 1 denotes a conductive base plate which is formed as a conductive layer by coating a thin metallic film by means of vacuum evaporation or the like on a supporting substance which consists of a metal plate or a macro-molecular compound or the like. The supporting substance being selected as required as either a flexible type or a rigid type.

Reference numeral 2 denotes a thin photoconductor layer with low sensitivity, which forms a high rectifying barrier by keeping contact with a metal of the conductive base plate 1, and which is composed of a photo-semiconductor endowed with a function of preventing electric charges from migrating thereinto from base plate 1, and in a case where the metal of the base plate 1 is for example aluminum, the photo-semiconductor is, for example, non-crystalloid selenium.

Reference numeral 3 denotes a thin highly sensitive photoconductor layer which is formed in the shape of a lattice or mesh, on the low sensitive photoconductor layer 2 as shown in FIG. 1B. Where the low sensitive photoconducter layer 2 is for example a non-crystalloid selenium as aforesaid, most preferably layer 3 is a thin layer composed of a low resistant photoconductive substance like an alloy of selenium and tellurium, or As-Se, or Se-Sb, etc. A layer 4 formed on the high sensitive photoconductor layer 3 is an organic semiconductor layer which is capable of holding electric charges on the surface thereof and of which the primary objective is to provide a passage therethrough for photo-charge carriers which are generated within photoconductor layers 2 and 3. Layer 4 which does not need to generate photo-charge carriers by itself can be made from any photoconductive substance with low sensitivity. Therefore most appropriate are, for example, polyvinyl-carbazole, polyimid resin, polyvinyl-naphthalene, polyvinyl-malachite green, and the like.

In the photosensitive plate aforementioned, if interposed between the conductive base plate 1 and the photoconductor layer 2 thereon is a uniform thickness layer 5, as shown in FIG. 2A and 2B, made from a semiconductive substance which is endowed with a function which permits layer 5 to form a high rectifying barrier by keeping contact with a metal of the base plate 1, and which prevents electric charges from migrating thereinto from the base plate 1, the photoconductor layer 2 is capable of being made from such a photoconductive substance that is of a lower resistance and of a higher sensitivity. Also the photoconductor layer 3 which is formed thereon in a shape of a lattice or a mesh is capable of being formed to such a photoconductor layer that is adversely of a higher resistance and of a lower sensitivity in comparison with photoconductor layer 2. Further, the uniform photoconductor layer 2 is capable of being formed with a lower sensitivity in comparison with the photoconductor layer 3. In a case where the base plate 1 is made from for example, a metallic aluminum, interposed thereon is the thin layer 5 made from a chalcogen glass semiconductor such as a non-crystalloid selenium, As-S, Sb-S, and the like, and formed thereon is the uniform photoconductor layer 2, and further formed thereon is the photoconductor layer 3, of which sensitivity is different therefrom, and which is of the shape of a lattice or a mesh. Finally, coated thereon is the organic semiconductor layer 4 as aforementioned.

As the photosensitive plate in accordance with this invention is constituted as described hereinabove, describing now its functions with a reference to such an embodiment thereof as shown in FIG. 1, the highly sensitive photoconductor layer 3 is formed into a shape of a lattice or a mesh; accordingly, formed on the low sensitive photoconductor layer 2 is a combined lattice or a combined mesh consisting of portions formed of the highly sensitive photoconductor layer 3 and other portions not formed thereto. Now, assuming that the light decay characteristics thereof not formed as above are denoted by *a* and the light decay characteristics thereof formed as above are denoted by *b*, which have respective curves as shown in FIG. 4A, the surface potentials on the curve *a* and *b* are coincidental at the zero point of the exposed light quantity. However, as the exposed light quantity increases, the curve *b* decreases more rapidly than the curve *a*, and after the exposed light quantity increases beyond a definite value thereof, both surface potentials approach more closely to the zero line as seen in the graph. Therefore, if the difference between both surface potentials is taken up, the difference ΔV is gradually increased in accordance with the increase of the exposed light quantity, but after reaching a definite value thereof, it is decreased in with the increase of the exposed light quantity. Namely, the difference ΔV is very close to zero at the light and the dark areas, and has a maximum value at the half tone areas, as seen therein. Therefore, the photosensitive plate in accordance with this invention is composed of a multitude of micronized but aligned micro-portions thereof each of which is provided with either one of

two light decay characteristics which are different from each other as shown by the two curves *a* and *b*.

Consequently, this photosensitive plate forms as shown in FIGS. 3A, 3B and 3C, on its high potential parts at the dark areas, a potential pattern indicating potentials corresponding to the lattice or mesh points the surface potential difference of which is an absolute minimum, and on its half tone parts it forms a potential pattern indicating a large difference between its surface potentials. And also on the light parts of its background it forms a meshwork pattern indicating a potential difference which is substantially of zero value.

This ensures that the half tone parts only are resolved into an intense meshwork pattern so as to fully eliminate the edge effect by virture of the potential difference, thereby the half tones are capable of being reproduced with high fidelity. The dark parts of a a picture image are never overlapped with the meshwork pattern so that the contrast between the dark parts and light parts is never lowered.

According to the invention as described hereinabove, the meshwork resolving function is electrically held in the interior of the photosensitive plate, it is not required therefore to form an optical meshwork separately, and as the meshwork resolving function is coated by the organic photo-semiconductor, it is never damaged mechanically so that the meshwork resolving function can be maintained for a long period, as well as the maintenance and handling thereof is facilitated thereby. Moreover, the meshwork resolving intensity is rich at the half tone parts which are hard to reproduce, enabling the reproduction thereof to be carried out with fidelity. Whereas, it is rarely shown on the background parts, enabling it to completely shut out contamination and fog from the background parts, while the meshwork resolving intensity is poor even at the dark parts, causing no lowering of the contrast thereat. These meshwork resolving intensities are capable of being controlled so as to be responsive to the sensitivity difference between both photoconductor layers **2** and **3**, as well as a pattern in the shape of a lattice or a mesh is capable of being easily formed by means of vacuum evaporation by making use of a high mesh screen, making it possible thereby to reproduce the half tones with high resolving power. As a result there is produced various effects which can not be obtained by any conventional photosensitive plate.

Hereinafter, several photosensitive plates which are manufactured in accordance with this invention will be described.

Example I

This example is of a photosensitive plate corresponding to the first embodiment, wherein a polyester film with a thickness of μ was purified in a vacuum of 10^{-3} mm Hg by ion bombardment for 30 – 60 seconds. Then it was placed in a vacuum of 10^{-5} - 10^{-6} mm Hg in order to form thereon a very thin film layer of Al_2O_3 in such a manner that a thin film of aluminum is first vacuum evaporated thereon to **10%** of its penetration factor. Secondly the vacuum evaporated aluminum layer was oxidized so that the Al_2O_3 layer was completed. Next, selenium having a purity of more than 99.99% is placed in a vacuum of about 10^{-5} mm Hg and was vacuum evaporated to a thickness less than 1 μ, so that the layer **2** was completely formed. After a screen of 200 mesh made of a stainless wire was closely attached thereonto, selenium of 99.999% purity was mixed with tellurium of 99.999% purity in a weight ratio of 20% and the mixture was sealed in a vacuum in which it was heated by an air furnace to a temperature of about 450°C – 500°C to mix and stir it up for **1** hour. The heated mixture was then cooled very rapidly to complete a Se-Te alloy which was thereafter vacuum evaporated in a vacuum of about 10^{-5} mm Hg to a thickness of about 1 μ, and when completed, the metal screen attached thereto was carefully removed so that the micronized layer **3** composed of a Se-Te alloy in a shape of a meshwork was completed.

An aqueous organic semiconductor consisting of components shown in the table below was coated thereon by means of a doctor or a roll to a thickness of 80 μ and the coating was dried for about 1 hour in a temperature of about 40°C so that the layer **4** of a thickness of 8 μ was completed. A photosensitive plate covered by a dried membrane of layer **4** was thus manufactured.

Table

Component	Weight (part)
Polyvinylcarbazol	100
Diphenyl Trichloride	40
Monochlorobenzen	1000

This photosensitive plate was charged to its surface potential of −600V by means of a corona discharge device, and by projecting a positive slide by means of an enlarger using a tungsten-filament lamp of 2800°K as its light source, the photosensitive plate was exposed for **1** second to light rays of an image with the illumination of 12 lux at its lightest part. Then it was developed by a magnet brushing method by means of a well regulated toner of micro particles. As a result there was obtained a visible image of an extremely high resolving power and with its half tone portions reproduced with fidelity.

Example II

This example also corresponds to the first embodiment, wherein used was a conductive base plate composed of a glass for use as a photographic plate with a thickness of 2 mm and aluminum with its light penetrating factor of 50% having been vacuum evaporated on the glass. Layer **2** was formed by vacuum evaporating a layer of As_2S_3 onto the base plate to a thickness of less than 1μ. Next, a meshed metal screen of 400 mesh made of a stainless wire was closely attached to layer **2** and a Se-Te alloy containing tellurium with a weight ratio of 10% was vacuum evaporated thereon to a thickness of 0.8μ so that layer **3** in a mesh-like shape was completely formed. Thereafter an aqueous organic semiconductor with the identical components shown in the table above was coated thereon in the same way as in example I so as to obtain a dired film thickness of 10μ and thereby to form the completed layer **4** and a complete photosensitive plate.

After having the surface of the photosensitive plate charged to −800V, a positive image having an illumination of 12 lux at its lightest part was projected thereon for 1 second. Then an electrostatic transfer sheet coated thereover with a vinylchloride acetate copolymer film of a thickness of 5μ was closely attached thereon, and they were pressed together by a grounded

roller from their rear side so that they were adhered to each other. Next, the transfer sheet was separated from the photosensitive plate and developed by a liquid developing method, a clear visible image which was completely free from background contamination and of which the half tone was reproduced with fidelity having been thereby obtained.

Example III

This example is a photosensitive plate corresponding to the second embodiment, wherein after polishing the surface of an aluminum plate of a thickness of 3 mm by means of a powder puff, the plate was washed by means of trichloroethylene, stiffly coated with a very thin layer of an Al_2O_3 membrane formed by the anodic oxidation method. Then the layer 5 consisting of a selenium layer was formed thereon to a thickness of 0.5 μ by a vacuum evaporation method, thereafter the layer 2 was formed thereon to the thickness of 0.8 μ by evaporting a Se-Te alloy containing telunium as 30% by its weight ratio in a vacuum. A metal net of 400 mesh made of a stainless wire was closely attached thereon, then the layer 3 was obtained by the formation of a Se-Te layer of a thickness of 0.8 μ by evaporating a Se-Te alloy containing telunium as 30% by its weight ratio in a vacuum. Finally an aqueous organic semiconductor substance shown in the table of Example I was coated thereon so as to make up a dried membrane thickness of 10 μ.

This photosensitive plate was charged to −1000V by means of a corona discharge device, and exposed for 0.3 seconds to light rays of a positive image with an illumination of 12 lux at its lightest part. The latent image formed thereby in the photosensitive plate was transferred to an electrostatic transfer sheet and developed by a liquid developing method to form a clear visible image which was completely free from background contamination and of which the half tone was very good having been obtained on the transfer sheet.

Additionally, in this example, the semiconductor layer was formed on the photoconductor layers, and the sensitivity of the uniform photoconductor layer 2 was made higher than that of the photoconductor layer 3. Therefore any image is represented by the identical group of points, however, if both sensitivities thereof are inverted so as to get an adverse relationship therebetween which is capable of being formed in the same way as aforesaid, the image reproduced as above will be represented by a linear meshwork.

We claim:

1. An electrophotographic sensitive plate for improving the fidelity of half-tone image reproduction, comprising:
- a conductive substrate;
- a first photoconductive selenium layer having a thickness of less than 1 micron deposited on said substrate for forming a rectifying barrier preventing the injection of charges from said substrate;
- a second photoconductive layer formed on said first photoconductive layer in a reticulated pattern having a thickness no greater than 1 micron and comprising a mixture of selenium with an element selected from the group consisting of Te, As and Sb and containing between 10 and 30 percent of said element by weight;
- a transparent organic semiconductor layer formed on said second photoconductive layer and comprising polyvinyl carbazole for maintaining electric charges on its surface and for transporting photocharge carriers generated within said first and second photoconductive layers.

2. An electrophotographic sensitive plate for improving the fidelity of half-tone image reproduction, comprising:
- a conductive substrate including a semiconductor layer of selenium deposited thereon having a thickness of less than 1 micron to provide a rectifying barrier preventing the injection of charges from said substrate;
- a first photoconductive layer having a thickness of no greater than 1 micron formed on said semiconductor layer and comprising a mixture of selenium and an element selected from the group consisting of Te, As and Sb and containing between 10 and 30 percent of said element by weight;
- a second photoconductive layer having a thickness of no greater than 1 micron formed on said first photoconductive layer in a reticulated pattern and comprising a mixture of selenium and an element selected from the group consisting of Te, As and Sb with the amount of the selected element in said second photoconductive layer less than the amount of the selected element in said first photoconductive layer;
- a transparent organic semiconductor layer formed on said second photoconductive layer and comprising polyvinyl carbazole.

3. An electrophotographic sensitive plate as defined in claim 1, wherein said second photoconductive layer comprises a mixture of selenium and tellurium and containing approximately 20% of tellurium by weight.

4. An electrophotographic sensitive plate as defined in claim 1 wherein a 200 - 400 mesh screen is used for forming said second photoconductive layer in a reticulated pattern.

5. An electrographic sensitive plate for improving the fidelity of half-tone image reproduction, comprising:
- a conductive substrate;
- a first photoconductive layer having a thickness of no greater than 1 micron and comprising a mixture of selenium with an element selected from the group consisting of Te, AS and Sb and containing between 10 and 30 percent of said element by weight;
- a second photoconductive selenium layer having a thickness of less than 1 micron deposited on said first photoconductive layer in a reticulated pattern;
- a transparent organic semiconductor layer formed on said second photoconductive layer and comprising polyvinyl-carbazole for maintaining electric charges on its surface and for transporting photocharge carriers generated within said first and second photoconductive layers.

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