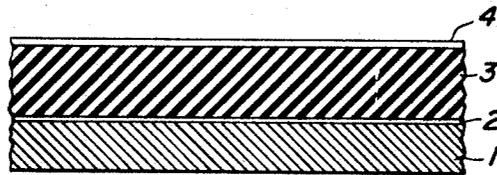


July 23, 1968

KATSUO MAKINO
ELECTROPHOTOGRAPHIC SENSITIVE MATERIAL CONTAINING
ELECTRON-DONOR DYE LAYERS
Filed March 1, 1965

3,394,001



INVENTOR.
KATSUO MAKINO

BY

Stanley Z. Lee

ATTORNEYS

1

2

3,394,001

ELECTROPHOTOGRAPHIC SENSITIVE MATERIAL CONTAINING ELECTRON-DONOR DYE LAYERS

Katsuo Makino, Odawara-shi, Japan, assignor to Xerox Corporation, Rochester, N.Y., a corporation of New York

Filed Mar. 1, 1965, Ser. No. 436,014

Claims priority, application Japan, Mar. 3, 1964, 39/11,554

16 Claims. (Cl. 96—1.5)

ABSTRACT OF THE DISCLOSURE

This invention relates to an electrophotographic plate comprising a conductive backing member, a boundary layer containing an electron-donor dye overlying said conductive backing member, a layer of photoconductive insulating material overlying said boundary layer and a surface layer containing an electron-donor dye overlying said photoconductive insulating layer. This plate is capable of imaging when charged either positively or negatively and produces copies having a minimum of powder-deficient spots.

BACKGROUND OF THE INVENTION

This invention relates to an electrophotographic sensitive material and, more particularly, to an improvement of a surface property of such a material in order to decrease defects, such as powder-deficient spots, in image quality.

In electrophotography, a coherent layer such as amorphous selenium or a dispersion of zinc oxide in an insulating resinous binder, is normally utilized. This layer is generally formed on a conductive supporting base and uniformly charged, as by corona charging. If the plate is stored in the dark, the charge will remain on the plate surface for a long time but will be instantly discharged in those portions of the plate surface which are light-exposed to sensitizing radiation. If the sensitizing radiation is applied in pattern form a latent electrostatic image comprising a corresponding charge pattern will be obtained. This latent electrostatic image can be developed with a colored particulate material. In direct development of the latent electrostatic image, the colored particulate material is charged to an opposite polarity as the charge comprising the latent image. The colored particulate material adheres electrically to those areas of the latent image which correspond to the dark areas in the document being copied. That is, the dark areas in the copy correspond to the dark areas in the original. Alternatively, the latent electrostatic image can be developed with a colored particulate material which is charged to the same polarity as the charge comprising the latent image. In such a development scheme, the colored particulate material adheres to the noncharged areas of the plate surface whereby the black and white areas of the original are reversed in the copy. This process is called reversal development. Other development processes are known, including cascade development, magnetic brush development, liquid development, etc. Such processes relate to the manner in which the developer is applied to the latent image supporting surface. In summary, past development, whether direct or reversal, has employed an electrostatic charge pattern on an electrophotographic surface and a charged particulate material. To change the character of the copy being produced (i.e., from direct to reversal or vice versa) a different powder, with or without carrier, charged to a different polarity from the first powder must be employed. This is a cumbersome inconvenience from a machine point of view.

The present invention is designed to eliminate the aforementioned inconvenience by improving the electrophotographic sensitive material itself. To date in the practice of electrophotography, amorphous selenium electrophotographic plates are uniformly positively charged whereas zinc oxide binder electrophotographic plates are uniformly negatively charged. When the aforementioned plates are charged to an opposite potential as specified in the preceding sentence, surface charge is not retained and the plate is unsuitable for the production of an acceptable copy in accordance with well known electrophotographic techniques.

An exemplary electrophotographic plate is produced by the deposition of amorphous selenium onto an aluminum backing member, the selenium and the aluminum being separated by an aluminum oxide interface. Such a plate can be easily uniformly positively charged and exhibits good sensitivity for the production of an electrophotographic copy. On the other hand, such a plate cannot be negatively charged and still be utilized to produce acceptable copies.

A further exemplary electrophotographic material is made by the dispersion of zinc oxide in an insulating resinous binder material. Normally, this dispersion is coated onto paper or other suitable backing material. Such a plate will accept a uniform negative charge and has sufficient electrophotographic sensitivity to produce an acceptable copy in accordance with known electrophotographic techniques. However, such a plate cannot be charged positively and utilized as such to produce acceptable copy.

The phenomena that a material can be uniformly charged to a first polarity but not a second polarity relates to its rectifying character, that is, it relates to a matter of injection of an electron from an adjacent conducting material. In other words, it relates to the surface characteristics of the photosensitive material or to a characteristic of a boundary layer disposed between the photosensitive material and the conductive supporting member.

By the present invention, however, the electrophotographic material can be charged either positively or negatively and, in accordance with well known electrophotographic techniques, can be utilized to produce an acceptable copy with either polarity charging. By controlling the polarity of the charge initially applied to the electrophotographic plate of the present invention, the nature of the copy (either direct or reversal) can be controlled without the necessity of changing the charge on the development material.

BRIEF DESCRIPTION OF THE INVENTION

Now, in accordance with the present invention, there is provided an electrophotographic plate comprising an electrically conductive backing member, a boundary layer overlying a surface of said backing member and including a quantity of electron-donor dye, a layer of photoconductive insulating material overlying said boundary layer, and an outer layer including a quantity of electron-donor dye overlying said layer of photoconductive insulator material. Thus, there is provided an electrophotographic plate having not only an electron-donor dye containing layer on its exposed surface but also a boundary layer of such material between the photoconductive insulating layer and its conductive supporting member.

By applying an electron-donor dye containing layer to the amorphous selenium surface, injection of a positive charge is retarded and positive chargeability of the surface is improved. Since injection is retarded, this also results in a decrease in the dark discharge rate. On the other hand, as a layer of electron-acceptor material is adhered to the photoconductive surface, injection of a

positive charge is enhanced with a resultant increase in the dark discharge rate.

The present invention will be described with reference to amorphous selenium as the photoconductive insulator material but it should be understood that this invention is not restricted to this material but is also applicable to other well known photoconductive insulators. Typical electron-donor dyes suitable for improving the surface character of the photoconductive insulator include methylene-blue, nigrosin, indigo-blue, Congo-red, etc. These materials can be dissolved in either an organic solvent or water or dispersed in an organic resinous material and applied to both surfaces of the photoconductive insulator material as the electrophotographic plate is formed.

Reference is now made to the figure wherein there is disclosed a cross-section of an electrophotographic plate. The plate comprises a conductive supporting member 1, a layer of photoconductive insulator material 3, and thin barrier layers 2 and 4 of an electron-donor dye containing material, said layers 2 and 4 being disposed on either side of photoconductive insulator layer 3.

By the use of layers 2 and 4, the photoconductive layer becomes symmetrical in both directions whereby the electrophotographic plate can be charged both positively and negatively. Though not intending to be limited by the following explanation, it is believed that positive hole injection from the treated free surface of the photoconductive material affects the chargeability in positive charging whereas positive hole injection from the boundary layer between the photoconductive layer and the substrate affects the chargeability in negative charging. Thus, it has been concluded that the boundary layer must be a barrier for positive hole injection. Further, if a symmetrical electrical construction is employed chargeability for both polarities should be approximately on the same order of magnitude.

The electrophotographic plate of the present invention can be formed by coating an electron-donor dye containing resin layer onto the conductive supporting material. Thereafter, the photoconductive insulator layer is deposited on the resin layer and, finally, a further layer of dye-containing resin is formed on the exposed surface of the photoconductive insulator. In this stage, the electron-donor dye can be applied in solution form.

As an alternate process, the photoconductive insulator layer can be formed on a temporary base. The electron-donor dye containing material is applied to the free surface of the photoconductive insulator layer and, thereafter, the treated surface is applied to the final supporting material. The temporary base is now stripped off the photoconductive insulator layer leaving a new exposed surface which also is treated as indicated above. The method of producing the electrophotographic plates of the present invention is not intended to be limited to the aforementioned processes, rather any suitable process can be utilized for this production.

Layers 2 and 4 are, in general, formed from the same material but different materials can be utilized provided they will give the same electrical effect to the photoconductive insulator layer. That is, each layer should include an electron-donor dye though, as indicated for this second embodiment, different dyes can be used in each layer. In this latter case, however, the electrical resistance of layer 2 should be lower than the relatively higher resistance of layer 4.

An amorphous selenium layer is deposited on an aluminum oxide layer of an aluminum plate to a thickness of 24 microns. The plate is charged to a positive potential by corona charging before and after the treatment of the plate by the immersion thereof into an isopropyl alcohol solution containing 0.05 percent nigrosin. Surface potentials are measured after 15 seconds charging where V max. is the maximum value obtained and V min. is the minimum value obtained.

The surface voltages of the material before and after treatment are as follows:

TABLE I

	Before Treatment		After Treatment	
	V max.	V min.	V max.	V min.
Sample:	<i>Volts</i>	<i>Volts</i>	<i>Volts</i>	<i>Volts</i>
1.....	237	129	520	150
2.....	286	206	533	529
3.....	231	145	522	515

As can be seen from Table I, V max. before treatment is much lower than after treatment. Additionally, the magnitude of the surface charge after treatment is much greater than before treatment. This means that the electrophotographic plate is electrically instable before treatment which results in powder deficient spots in the copies obtained. After treatment in accordance with the present invention, the aforementioned powder deficient spots cannot be found in copies produced either by direct or reversal development.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The following examples are given to enable those skilled in the art to more clearly understand and practice the invention. They should not be considered as a limitation upon the scope of the invention but merely as being illustrative thereof.

Example I

Nitrocellulose containing 0.05 weight percent nigrosin is coated on an aluminum plate and dried to a thickness of 1.5 micron. A 40 micron layer of amorphous selenium is deposited by vacuum evaporation onto the nitrocellulose layer. A second layer of the nitrocellulose-nigrosin material is coated onto the free surface of the amorphous selenium and dried to a thickness of 2 microns. A control material which eliminated the nitrocellulose-nigrosin layer on the aluminum plate was also produced.

When positively charged and developed, the two plates gave essentially the same results. In each instance, however, the plate having the nitrocellulose-nigrosin binder layer on both sides of the selenium layer was a superior plate in that less white spots in direct development and less black spots in reversal development were obtained.

When negatively charged with direct development, the plate of the present invention produced a copy having very few white spots in image areas whereas many more white spots appeared in the copy made from the reference material. In reversal development, the present invention produced a copy having very few black spots in image areas whereas the reference material produced a copy having so many black spots that it was totally unacceptable.

The results are shown in the following table:

TABLE II

	Positive Charge		Negative Charge	
	(A)	(B)	(A)	(B)
Invented Material..	No.....	No.....	Very few...	Very few.
Reference Material.	Very few...	Very few...	Many.....	Many.

(A) White spots in image areas in direct development.
(B) Black spots in image areas in reversal development.

While this visual comparison may seem to be a crude manner of analyzing the performance of the respective plates, it is, in essence, one way any copy is analyzed, that is, the copy is compared visually with the original and the mental image of what one would consider to be a perfect copy. In any event, the results show that the electrophotographic plate of the present invention is superior to the reference material both for positive and negative charging and for direct and reversal development.

The optical sensitivity of the treated plate with respect to the exposure necessary to reduce the surface potential to one-half its initial potential was about 2 lux.-sec. for positive charge and 20 lux.-sec. for negative charge.

Example II

A methacrylate lacquer containing 0.5 percent methylene-blue is coated on an aluminum plate and dried to a thickness of about one micron. A 60 micron layer of selenium containing 5 percent tellurium is deposited on the dye-containing methacrylate layer. Finally, a layer of 20 weight percent nitrocellulose and 80 weight percent cellulose acetate containing 0.07 weight percent nigrosin is applied to the free surface of the selenium-tellurium layer and dried to a thickness of 1.7 microns. The electro-photographic plate thus made has nearly the same chargeability for positive and negative charging. Its sensitivities with respect to the exposure necessary to reduce the surface potential to one-half of its initial potential were 0.7 lux-sec. for positive charge and 20 lux-sec. for negative charge. Spots or other image defects were not observed in copies made from negative and positive charging with either direct or reversal development.

Example III

The porous aluminum oxide layer formed on an aluminum plate was treated with a solution of Congo-red. After the treatment, a 50 micron layer of a selenium-tellurium alloy was coated by vacuum evaporation onto the treated surface. The plate thus obtained was immersed into a solution of isopropyl alcohol containing 0.002 percent nigrosin. The nigrosin was absorbed into the photoconductive layer. This plate had substantially the same chargeability for positive and negative charging and its sensitivity was similar to the plate produced in Example II. However, a few white spots in direct development and a few black spots in reversal development were found even though the copies were much improved over copies obtained with the reference material of Example I.

I claim:

1. An electrophotographic plate comprising a conductive backing member, a boundary layer containing an electron-donor dye overlying said conductive backing member, a layer of photoconductive insulating material overlying said boundary layer and a surface layer containing an electron-donor dye overlying said photoconductive insulating layer.

2. The electrophotographic plate of claim 1 wherein said electron-donor dye has pi electrons and non-bonded electrons available for coordination.

3. The electrophotographic plate of claim 1 wherein the photoconductive insulating material is amorphous selenium.

4. The electrophotographic plate of claim 1 wherein the photoconductive insulating material is an alloy of selenium with tellurium.

5. The electrophotographic plate of claim 4 wherein said alloy contains about 5% tellurium.

6. The electrophotographic plate of claim 1 wherein the photoconductive insulating layer comprises a particulate photoconductive material dispersed throughout an insulating resinous binder.

7. The electrophotographic plate of claim 6 wherein the particulate photoconductive material is zinc oxide.

8. The electrophotographic plate of claim 1 wherein said electron-donor dye is selected from the group consisting of methylene-blue, nigrosin, indigo-blue, and Congo-red.

9. The electrophotographic plate of claim 1 wherein the electron-donor dye in said boundary layer differs from the electron-donor dye applied to the free surface of said photoconductive insulator layer.

10. The electrophotographic plate of claim 1 wherein the electron-donor dye in each dye-containing layer is the same.

11. The electrophotographic plate comprising a conductive supporting substrate, a boundary layer containing nigrosin overlying said conductive substrate, a layer of amorphous selenium overlying said nigrosin-containing layer and a second nigrosin-containing layer overlying said selenium layer.

12. An electrophotographic plate comprising a conductive substrate, a boundary layer containing methylene-blue overlying said conductive substrate, a layer of an alloy of selenium and tellurium overlying said methylene-blue-containing layer, and a layer containing nigrosin overlying said selenium-tellurium alloy layer.

13. An electrophotographic plate comprising a conductive backing member, said backing member having a surface thereof treated with a solution of Congo-red, a layer of an alloy of selenium and tellurium overlying said treated surface, and a surface layer containing nigrosin overlying said alloy layer.

14. An electrophotographic plate comprising a conductive backing member, a boundary layer containing an electron-donor dye overlying said conductive backing member, a layer of photoconductive insulating material overlying said boundary layer, said photoconductive insulating layer having the free surface thereof treated with an electron-donor dye containing material.

15. An electrophotographic plate comprising a conductive backing member, one surface of said conducting backing member having been treated with an electron-donor dye containing material, a layer of photoconductive insulating material overlying said treated surface, and an electron-donor dye containing material surface layer overlying said photoconductive insulating layer.

16. An electrophotographic plate comprising a conductive backing member, one surface of said backing member having been treated with an electron-donor dye containing material, a layer of photoconductive insulating material overlying said treated surface, said photoconductive insulating layer having the free surface thereof treated with an electron-donor dye containing material.

References Cited

UNITED STATES PATENTS

2,901,348 8/1959 Dessauer et al. ----- 96-1.5

NORMAN G. TORCHIN, *Primary Examiner.*

J. C. COOPER III, *Assistant Examiner.*