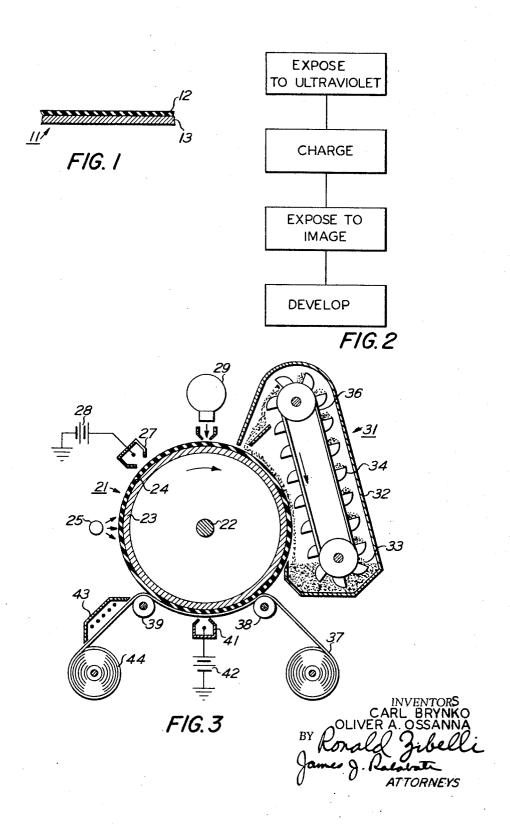
# ELECTROPHOTOGRAPHIC IMAGING PROCESS

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3,445,225
ELECTROPHOTOGRAPHIC IMAGING PROCESS
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4 Claims

# ABSTRACT OF THE DISCLOSURE

This application relates to electrostatic and photoconductographic imaging methods featuring an imaging member comprising from about 2-35% by weight of the open, 15 excited form of a spiropyran in an aromatic organic photoconductive insulating material.

This invention relates in general to a novel photoconductive material and process and more specifically to a photoconductive material and process in which ultraviolet irradiation is employed to sensitize the photoconductive material.

Heightened interest has recently developed in photoconductive materials tailored for specific end uses. This interest has, of course, largely been generated by the recent market growth for photocells, television pickup tubes, office copying machines and photographic systems 30 and other devices making use of these photoconductive materials.

Xerographic copying, for example, has undergone an extremely large growth in the past few years. In this copying technique, as originally disclosed by Carlson in 35 U.S. Patent No. 2,297,691, a photoconductive insulating layer making up part of a xerographic plate is generally first given a uniform electrostatic charge over its entire surface to sensitize it and is then exposed to an image of activating electromagnetic radiation such as light, X-ray or the like which selectively dissipates the charge in illuminated areas of the photoconductive insulator, leaving behind charge in the non-illuminated areas to form a latent electrostatic image. The latent image is then developed, or made visible, by the deposition of finely di-vided, electroscopic marking material on the surface of the photoconductive insulating layer as a result of which the marking material conforms to the pattern of the latent image. Where the photoconductive material is reusable, the visible image of powdered marking material is then transferred to a second surface such as paper, plastic or the like and then fixed in place to form a permanent, visible reproduction of the original. Where, on the other hand, a less expensive, non-reusable photoconductive material is employed, the toner particles are fixed in place directly on its surface with the consequent elimination of the transfer step from the process. Where the photoconductor itself is optically transparent it has been contemplated for use as a projection transparency after the toner image has been fixed on its surface. With a non-reusable photoconductor which is not transparent, it is desirable that the photoconductor be light in color so as to provide strong contrast with the dark colored developer particles for easy viewing. The use of photoconductors having these characteristics has often been frustrated in the past by the fact that most of the known non-reusable photoconductors, including organic materials such as anthracene, polyvinylcarbazol, thiazoles, oxadiazoles, etc., must be dye sensitized to have adequate sensitivity to visible light or other desirable radiation sources so that their photographic speeds will be commercially acceptable. The

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use of these sensitizing dyes colors the photoconductors, decreasing their transparency and reducing contrast with the developed image areas or at least imparting a displeasing off-white cast to these materials when the dyes are used even in low concentrations.

Other photoconductors, both reusable and non-reusable, which have adequate sensitivity without dye sensitization such as amorphous selenium, cadmium sulfide and the like have inherent color of their own which frequently makes them unsuitable for the aforementioned applications. These photoconductors frequently suffer from the same deficiencies when they are employed in other imaging systems such as electrostatically induced plastic deformation imaging and electrolytic imaging where exposure of the photoconductor is employed either to control the charge pattern laid down on a thermoplastic prior to softening so that the charge can deform the plastic in charged areas or where the exposure of the photoconductor is used in the electrolytic system to control the conductivity of the photoconductive surface which makes up one electrode and an electrolytic imaging cell. Reference is made to a text entitled "Xerography and Related Processes" by J. H. Dessauer and H. E. Clark, copyright 1965 by the Focal Press Limited, which contains a very detailed description of the xerographic process as well as descriptions of the thermoplastic deformation imaging process on pages 375-388 and the electrolytic imaging process of pages 461-462.

It is accordingly an object of this invention to provide a new photoconductive material.

It is a further object of this invention to provide a novel sensitizing agent for photoconductors.

A still further object of the invention is to provide for a novel photosensitizing dye for photoconductors which can be converted to a colorless condition after the photoconductor has been used.

Yet another object of this invention is to provide a novel imaging process.

It is also an object of this invention to provide visible light sensitive photoconductor whose sensitivity can be modified by ultraviolet light exposure.

These and still further objects of the invention are accomplished, generally speaking, by combining photochromic spiropyran compounds in an imaging layer with an organic photoconductor and then uniformly exposing this imaging layer to ultraviolet radiation prior to its use as a visible light photoconductor. A binder may also be employed in the imaging layer to form a three-component system; however, it has been found that aromatic, natural and synthetic resins which are not ordinarily thought of as photoconductors have sufficient photoconductivity to act as the photoconductive component itself when sensitized with the spiropyran compounds of this invention. Where desired, however more sensitive materials ordinarily thought of as organic photoconductors may also be mixed in the imaging layers to form a three-component system. Other resins, plasticizers, pigments, dyes, sensitizers, synergizing agents and the like may also be employed in the imaging layer to improve its performance for various specific end uses.

In order that the invention will be more clearly understood, reference is now made to the accompanying drawings in which an embodiment of the invention is illustrated by way of example and in which:

FIGURE 1 is a side sectional view of an imaging member made according to the invention;

FIGURE 2 is a flow diagram of the process steps of the invention; and,

FIGURE 3 is a side sectional view of an illustrative embodiment of an apparatus adapted for imaging according to the invention.

Referring now to FIGURE 1, there is seen an imaging member generally designated 11 made up of the photoresponsive layer 12 on a supporting substrate 13. It is to be understood that supporting substrate 13 is shown by way of example only and is no way essential to the operation of the photoconductive layer, especially when this layer has sufficent mechanical strength to be self-supporting. When the photoconductive material is used in the xerographic process, it is often convenient to employ a congold, optically transparent layers of tin oxide, gold, copper iodide or copper oxide on glass or the like so that the substrate will provide both mechanical strength to the imaging layer and will also serve as a conductive ground plane to facilitate electrical corona charging of 15 the imaging member during the process as more fully described hereinafter. On the other hand, if two-sided corona charging as described, for example, in U.S. Patent No. 2,922,883, is employed in the xerographic process, the substrate may be omitted since this charging technique 20 does not require a ground plane in the xerographic plate. A conductive substrate may also be desirable for use in other processes such as the electrostatically induced plastic deformation process or electrolytic imaging process described above. When the photoconductor is employed as a 25 photocell (photoresponsive resistor) in an electrical circuit, it may be desirable to provide the photoconductive layer with two electrically separate conductive contacts either on opposite sides of the photoconductive layer or at spaced positions on one surface of the photoconductor.

The percentage of photochromic spiropyran compounds in photoconductive layer 12 is not critical and may, for example, range from about 35% by weight down to about 2% by weight of the total layer; however, best results are produced using a range of from about 10-20%. Any suit- 35 able photochromic spiropyran may be employed. Typical photochromic spiropyrans include:

1,3,3-trimethyl-6'-nitro-8'-allylspiro (2'H-1'-benzopyran-2,2'-indoline);

1,3,3-trimethyl-5,6'-dinitro-spiro (2'H-1'-benzopyran-2,2'-indoline);

1,3,3-trimethyl-7'-nitro-spiro (2'H-1'-benzopyran-2,2'indoline);

3-methyl-6-nitro-spiro[2H-1-benzopyran-2,2'-(2'H-1'beta-naphthopyran)];

1,3,3-trimethyl-8'-nitro-spiro (2'H-1'-benzopyran-2,2'-

indoline); 1,3,3-trimethyl-6'-methoxy-8'-nitro-spiro (2'H-1'-benzo-

pyran-2,2'-indoline); 1,3,3-trimethyl-5 chloro-5' nitro-8'-methoxy-spiro (2'H-1'-

benzopyran-2,2'-indoline); 1,3-dimethyl-3-isopropyl-6' nitro-spiro (2'H-1'-benzo-

pyran-2,2'-indoline); 1-phenyl-3,3-dimethyl-6'-nitro-8'-methoxy-spiro (2'H-1'-

benzopyran-2,2'-indoline); 7'-nitro-spiro-[xantho-10,2' (2'H-1'-benzobetanaphtho-

pyran)]; 3,3'-dimethyl-6'-nitro-spiro (2'H-1'-benzopyran-2,2'-

benzo-thiazole); 3,3'-dimethyl-6'-nitro-spiro (2'H-1'-benzopyran-2,2'-

benzo-oxazole); 1,3,3-trimethyl-6'-nitro-spiro (2'H-1'-benzopyran-2,2'-

indoline);

6'-nitro-8'-methoxy-1,3,3-trimethylindolinobenzopyrylospiran;

6'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;

8'-allyl-3,3-trimethylinodlinobenzopyrylospiran;

8'-carbomethoxy-1,3,3-trimethylinodlinobenzopyrylo-

8'-methoxy-1,3,3-trimethylindolinobenzopyrylospiran;

6',8'-dinitro-1,3,3-trimethylinodlinobenzopyrylospiran; 7'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;

8'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;

6',8'-dibromo 1,3,3-trimethylindolinobenzopyrylospiran;

6'-chloro-8'-nitro-1,3,3-trimethylindolinobenzopyrylo-

5-nitro-6'-nitro-1,3,3-trimethylindolinobenzopyrylospiran; 6'-nitro-8'-fluoro-1,3,3-trimethylindolinobenzopyrylospiran;

6'-methoxy-8'-nitro-1,3,3-trimethylindolinobenzopyrylospiran;

5'-nitro-8'-methoxy-1,3,3-trimethylindolinobenzopyrylospiran:

ductive substrate such as copper, brass, aluminum, silver, 10 and 6'-bromo-8'-nitro-1,3,3-trimethylindolinobenzopyrylospiran and mixtures thereof.

> Any suitable organic photoconductor containing at least one aromatic group may be employed in the photoconductive layer 12 in conjunction with the photochromic spiropyran, including even those organic photoconductors with extremely low levels of photosensitivity prior to their combination with the spiropyran. Typical organic photoconductors include phenol-formaldehyde polymer, rosin modified phenol-formaldehyde polymer, styrene butadiene copolymer, polyalphamethyl styrene, the glycerol ester of 50% hydrogenated abietic acid, polyvinyl toluene, polyvinyl naphthalene, polyvinyl carbazole, coumarone-indene polymers, polycarbonates, polyurethanes, epoxies, phenoxies,

4,5-diphenylimidazolidinone;

4,5-diphenylimidazolidinethione;

4,5-bis-(4'-amino-phenyl)-imidazolidinone;

1,5-cyanonaphthalene;

1,4-dicyanonaphthalene; aminophthalodinitrile;

nitrophthalidinitrile;

1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8);

3,4-di-(4'-methoxyphenyl)-7,8-diphenyl-1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8);

3,4-di-(4'-phenoxy-phenyl)-7,8-diphenyl-1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8);

3,4,7,8-tetramethoxy-1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8);

40 2-mercapto-benzthiazole;

2-phenyl-4-diphenylidene-oxazolone;

2-phenyl-4-methoxy-benzylidene-oxazolone;

6-hydroxy-2-phenyl-3-(p-dimethylamino phenyl)benzofurane;

45 6-hydroxy-2,3-di-(p-methoxyphenyl)-benzofurane;

2,3,5,6-tetra-(p-methoxyphenyl)-furo-(3,2f)-benzofurane; 4-dimethylamino-benzylidene-benzhydrazide;

4-dimethylaminobenzylideneisonicotinic acid hydrazide; furfurylidene-(2)-4'-dimethylamino-benzhydrazide;

5-benzilidene-amino-acenaphthene;

3-benzylidene-amino-carbazole;

(4-N,N-dimethyl-amino-benzylidene)-p-N,N-dimethylaminoaniline:

(2-nitro-benzylidene)-p-bromo-aniline;

N,N-dimethyl-N'-(2-nitro-4-cyano-benzylidene)-pbromo-aniline;

N,N-dimethyl-N'-(2-nitro-4-cyano-benzylidene)-pphenylene-diamine;

2,4-diphenyl-quinazoline;

2-(4'-amino-phenyl)-4-phenyl-quinazoline;

2-phenyl-4-(4'-dimethyl-aminophenyl)-7-methoxyquinazoline;

1,3-diphenyl-tetrahydroimidazole;

1,3-di-(4'-chlorophenyl)-tetrahydroimidazole;

65 1,3-diphenyl-2,4'-dimethylaminophenyl)-tetrahydroimidazole;

1,3-di-(p-tolyl)-2-[quinolyl-(2'-)]-tetrahydroimidazole;

3-(4'dimethylaminophenyl)-5-(4"-methoxyphenyl-6phenyl-1,2,4-triazine;

70 3-pyridil-(4')-5-(4"-dimethylaminophenyl)-6-phenyl-1,2,4-triazine:

3,(4'-aminophenyl)-5,6-diphenyl-1,2,4-triazine;

2,5-bis[4'-aminophenyl-(1')]-1,3,4-trizole;

2,5-bis [N-ethyl-N-acetyl-amino)-phenyl-(1')]-1,3,4-

75 triazole: 5

1,5-diphenyl-3-methyl-pyrazoline;

1,3,4,5-tetraphenyl-pyrazoline;

1-methyl-2-(3',4'-dihydroxy-methylene-phenyl)benzimidazole;

2-(4'-dimethylamino phenyl)-benzoxazole;

2-(4'-methoxyphenyl)-benzthiazole;

2,5-bis-[p-aminophenyl-(1)]-1,3,4-oxidiazole;

4,5-diphenyl-imidazolone;

3-aminocarbazole;

copolymers and mixtures thereof.

There is shown in FIGURE 2 a complete set of process steps for using the photoconductive material of this invention in xerographic imaging. The first step of this process involving uniform exposure to ultraviolet light or any other suitable actinic radiation source capable of converting at least a portion of the photochromic spiropyran molecules from the closed, unexcited form to the excited open form is shown in the following typical reaction:

where  $\delta^+$  and  $\delta^-$  are partial charges.

Although the process steps illustrated in FIGURE 2 are typical of one process in which the photoconductor is employed, only this ultraviolet light exposure step is the one which is commonly utilized in activating the photoconductor to visible light sensitivity for use in any process. It is believed that after conversion of the photochromic spiran compound from the closed, unexited form to the open excited form that they form a highly, photosensitive charge transfer complex with the photoconductor initially included in the imaging layer. In the original colorless form of the photochromic spiran the two moieties of the molecule bridged by the spiro carbon are in planes that are perpendicular. This arrangement prevents a strong  $\pi$  bond overlap with the aromatic groups in the photoconductor. When the spiropyran molecule is exposed to ultraviolet light, the pyran ring is ruptured and the spiro carbon assumes a trigonal valency state that enables both parts of the molecule to assume a common plane and establish resonance throughout the molecule. Once the molecule has assumed this planar configuration,  $\pi$  bond overlap with the host photoconductors' aromatic groups is greatly enhanced and, as a result, a much more effective charge transfer complex is formed.

As stated above, once conversion to the higher photochromic form is completed as by ultraviolet exposure, the photoconductive charge transfer complex which is believed to be formed can be used as a sensitive photoconductor in many applications. In the xerographic application, as illustrated in the process steps of FIGURE 2, however, ultraviolet exposure is followed by charging uniformly the exposed surface of the imaging layer, exposing the uniformly charged layer to the pattern to be reproduced with a light source which radiates at least in the visible light range (from about 4,000 to 7,500 angstrom units 70 wavelength) and then developing the latent electrostatic image left behind after exposure with finely divided electroscopic marking particles. Any suitable electrostatic charging technique may be employed to carry out the charging step. Typical of these are corona discharges de6

scribed in U.S. Patents 2,588,699 to Carlson; 2,836,725 to Vyverberg and 2,777,957 to Walkup; induction charging as described in U.S. Patent 2,833,930 to Walkup and triboelectric charging by surface rubbing as described in U.S. Patent 2,297,691 to Carlson. Various development techniques may also be employed for developing the latent image produced by the charging and exposure steps. Typical of these are cascade development, as described in U.S. Patents 2,618,551 and 2,618,552; magnetic brush development as described in U.S. Patent 3,015,305 to Hall; touchdown and skid development as described in U.S. Patent 2,895,847 to Mayo; powder cloud development as described in U.S. Patent 2,918,910 to Carlson; liquid spray development as described in U.S. Patent 2,551,582 to Carlson, immersion development as described in U.S. Patent 2,907,674 or any one of a number of other development techniques conventionally used in the xerographic art. Once development has been completed the developed image may either be fixed in place on the surface of the imag-20 ing layer or transferred to a second surface or transfer sheet and fixed thereon so that the imaging layer can be reused. Transfer of the developer pattern from the imaging layer to a transfer sheet may be accomplished by any suitable technique such as electrostatic attraction as de-25 scribed in U.S. Patent 2,576,047 to Schaffert or by coating the transfer sheet with an adhesive for the developer material or the like. Fixing of the developer to the surface upon which it is to finally reside may be carried out by heating, subjecting the surface to a solvent vapor atmosphere, overcoating or other techniques. In the event that the image is to be fixed directly on the surface of the imaging member and it is desired to use it as a transparency the photochromic spiropyran in the imaging member may be simply allowed to revert to a colorless or less intensely colored form in room light or this process may be accelerated by exposing the imaging layer uniformly to a yellow light source or heat.

In FIGURE 3, there is illustrated a simple exemplary apparatus for carrying out the imaging technique of the invention. This apparatus consists of a cylindrical imaging drum 21 mounted for rotation about a horizontal axis 22. The drum 21 comprises a supporting metal substrate 23 and a photoconductive layer 24 made up of a photochromic spiropyran and organic aromatic photoconductor of the type described supra. Although the particular substrate material used is aluminum, any one of a number of other suitable materials may be employed. It is also to be noted that although the drum is in the form of a rigid cylinder, it may take many other shapes including that of a flat plate, a polygon, an ellipse or the like and may be flexible as well as rigid. As the drum rotates in the direction indicated by the arrow, it is first uniformly exposed with an ultraviolet light source 25 to convert the spiropyran to its open form so that it will form a highly sensitive photoconductive charge transfer complex with the organic photoconductor. After ultraviolet exposure, the drum passes beneath a charging unit 27 connected to a source of high potential 28. The charging unit contains one or more wire filaments which are connected to the potential source and operates on the corona discharge technique as described above. Essentially, this technique consists of spacing a filament slightly from the surface of the drum with a conductive base of the drum grounded and applying a high potential to the filaments so that a corona discharge occurs between the filament and the drum thereby serving to deposit charged, ionized air molecules on its surface and raising its level of potential with respect to ground. The photochromic layer on the drum will hold its charge owing to its relatively high level of resistivity. As the drum continues to rotate at a uniform velocity, it passes beneath a visible light projector 29 which exposes the charged surface to the image to be reproduced. This exposure step serves to dissipate charge from areas of the layer which are exposed to light resulting in a residual charge pattern corresponding to the original image pro-

jected. The latent image formed by the charging and exposure stations of the apparatus on the drum surface then moves past a developing unit generally designated 31. The illustrated developing unit is of the cascade type which includes an outer container or cover 32 with a trough at its bottom containing a supply of developing material 33. The developing material is picked up from the bottom of the container and dumped or cascaded over the surface by a number of buckets 34 on an endless driven conveyor belt 36. This development technique, which is more fully described in the patents supra, utilizes a two-element developing mixture including toner particles and larger carrier beads which serve to deagglomerate the toner particles and to charge them by virtue of rubbing together of carrier and toner in the apparatus. When the beads with the 15 toner particles clinging to them are cascaded over the drum surface the electrostatic field from the charge pattern on the drum pulls toner particles off the carrier beads serving to develop the pattern. The carrier beads, along with any other toner particles not used to develop the 20 image, then fall back into the bottom of container 32. Once development has taken place, the drum bearing the developed powder image moves around until it comes in contact with a copy web 37 which is pressed up against the drum surface by two idle rollers 38 and 39 so that the 25 web moves at the same speed as the periphery of the drum. A transfer unit 41 is placed behind the web and spaced slightly from it between the rollers 38 and 39. This unit is similar in principle to the charging mechanism 27 and 28 and also operates on the corona discharge principle. The 30 transfer unit is connected to a source of high potential 42 of the same polarity as that employed in the charging unit 27 so that it deposits charge on the back of web 37 which is of the same polarity as the charge pattern on imaging layer 21 and is opposite in polarity of the charge on toner particles used in developing the plate. As more fully described in U.S. Patent 2,576,047, the application of this corona discharge on the back of the web serves to transfer the developed toner particle image from the surface of the drum to the web. Once the toner image has been 40 transferred, the web separates from contact with the drum and passes beneath a radiant heat fixer 43 which fuses the toner particles to the web whereupon it is wound up on a takeup reel 44 and the drum is ready for a new cycle of operation.

In the event that a non-reusable photoconductor is employed, an apparatus similar to that described in FIGURE 3 can be used except that the transfer station is eliminated from the device and the photoconductor is provided in continuous web form or single sheet form rather than in 50 the form of a rotatable drum made as a fixed part of the machine.

The following illustrative examples of preferred embodiments of the invention are now given to enable those skilled in the art to more clearly understand and practice 55 the invention. Unless otherwise indicated, all parts and percentages are taken by weight.

## Example I

One gram of 6'-nitro-1,3,3-trimethylindolinobenzopyrylospiran and 10 grams of polyalphamethyl styrene are dissolved in 90 grams of toluene and dip coated to a thickness of about 2 microns on two aluminum plates and air dried. One of the films is then charged in the dark for one minute to about 700 volts and the rate of its charge 65 decay is measured with a vibrating reed electrometer in the dark during a two-minute interval. After recharging, the surface of the sample is illuminated with visible light using a Bausch and Lomb microscope illuminator held at a distance of about 4 inches from the sample and the rate of discharge is measured with the same electrometer. The second film coated is pre-exposed to ultraviolet light using a one-minute exposure with a 9-watt fluorescent light available from the Eastern Corporation of Westbury, Long Island, sold under the trade name "Blacklite" using a filter

which passes about a 10 angstrom bandwidth centered on 3660 angstrom units. This produces a deep, maroon color in the film. The light and dark discharge rates of this film are also measured according to the same procedure used with the first film. Although both film samples hold an initial potential of about 700 volts, the dark and light discharge curves plotted as time vs. retained voltage show that the sample which is not pre-illuminated with ultraviolet light has light and dark discharge curves which are only separated by about 50 volts even after 60 seconds while the pre-exposed sample has dark and light discharge curves which are separated by well over 350 volts. Xerographic development of images confirm the much higher photoconductor response speed of the pre-exposed sample.

## Examples II-V

The procedure of Example I is repeated using the following photoconductors in place of the polyalphamethyl styrene of Example I; in Example II, Staybelite Ester 10, a glycerol ester of 50% hydrogenated rosin is employed; in Example III, Amberol F-71, a rosin modified phenolformaldehyde resin is employed; in Example IV, Piccodiene 2215, a styrene-butadiene copolymer is employed and in Example V, Amberol ST-137, an unmodified unreactive phenolformaldehyde resin is employed. In all instances, the light discharge curve of the ultraviolet preexposed sample goes well below that of the sample which is not pre-exposed to ultraviolet light and the initial rate of light discharge is steeper in the pre-exposed samples. Although Example V shows about equal sensitivity with that of Example I, the other samples are somewhat less sensitive.

# Examples VI-VIII

The procedure of Examples I, II and V is repeated except that the photochromic spiropyran is not included in the coating solution. Charging exposure and monitoring with the vibrating reed electrometer indicates that the resinous photoconductive materials employed in each coating show only an extremely small light response with their light exposed charge decay curves running only 5-10 volts below their dark decay curves.

## Examples IX-XIV

The procedure of Example I is repeated using the following photochromic compounds in place of the 6'-nitro-1,3,3-trimethylindolinobenzopyrylospiran; in Example IX the photochromic used is 1,3,3-trimethyl-6'-methoxy-8'nitrospiro (2'H-1'benzopyran-2,2'-indoline); in Example X the photochromic used is 1,3,3-trimethyl-5-chloro-5'nitro-8'-methoxy-spiro (2'H-1'-benzopyran-2,2'-indoline); in Example XI the photochromic used is 1-phenyl-3,3-dimethyl-6'-nitro-8'-methoxy-spiro (2'H-1'-benzopyran-2,2'indoline); in Example XII the photochromic used is 8'methoxy-1,3,3-trimethylindolinobenzopyrylospiran; in Example XIII the photochromic used is 6',8'-dibromo-1,3,3trimethylindolinobenzopyrylospiran and in Example XIV the photochromic used is 6'-chloro-8'-nitro-1,3,3-trimethylindolinobenzopyrylospiran. Each of these examples produce about equal results with those of Example I except for a slightly lower light sensitivity.

Although specific materials and conditions are set forth in the above examples, these are merely illustrative of the present invention. Various sets of materials, such as any of the typical photochromic and/or aromatic photoconductors listed above which are suitable, may be substituted for the materials listed in the examples with similar results. The film for this invention may also have other materials mixed, dispersed, copolymerized or otherwise added thereto to enhance, synergize, sensitize or otherwise modify the properties thereof. Many such modifications and/or additions to the process will readily occur to those skilled in the art upon reading this disclosure and these are intended to be encompassed within the spirit of the invention.

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The trivial name "spiropyran" as used throughout the specification and claims is employed as a shorthand term to encompass all of the photochromic compounds listed above.

What is claimed is:

1. A method of forming a latent electrostatic image comprising uniformly charging an imaging member comprising from about 2% by weight to about 35% by weight of the open, excited form of a spiropyran compound in an aromatic organic photoconductive insulator.

2. A method of xerographic imaging comprising uniformly charging a photoconductive insulating xerographic plate comprising from about 2% by weight to about 35% by weight of the open excited form of a spiropyran in an aromatic organic photoconductor, exposing said charged photoconductive insulator to a pattern with an actinic electromagnetic radiation source and developing the resulting latent electrostatic image with finely divided electroscopic marking material.

3. A method of imaging comprising uniformly charging a thermoplastic imaging member comprising from about 2% by weight to about 35% by weight of the open, excited form of a spiropyran compound blended with an aromatic organic photoconductive insulating material, exposing said imaging member to a pattern to be reproduced with an actinic electromagnetic radiation source and softening said thermoplastic imaging member

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to allow the electrostatic latent image field forces to deform said imaging member in image configuration.

4. A method of imaging comprising exposing an imaging member comprising from about 2% by weight to about 35% by weight of the open, excited form of a spiropyran compound blended with an aromatic organic photoconductor to a pattern to be reproduced with an actinic, electromagnetic radiation source, placing said imaging member in an electrolyte bath across from a conductive electrode and applying an electrical potential across said electrode and said imaging member, said potential being of a polarity to form an electrolytic deposit in image configuration on said imaging member.

# References Cited

#### UNITED STATES PATENTS

	3,100,778	8/1963	Berman 96—90 X
	3,287,121	11/1966	Hoegl 96—1.5
	3,322,678	5/1967	Dorion 252—300
20	3,364,023	1/1968	Becker et al 96—27

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