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METHOD OF CHARGING A ZINC OXIDE PHOTOCONDUCTIVE LAYER WITH A POSITIVE CHARGE

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ABSTRACT OF THE DISCLOSURE

A method of forming an image on a photosensitive zinc oxide binder layer which includes uniformly exposing the layer to a source of negative potential, followed by exposing the surface to a neutralizing source of positive potential resulting in the surface charge being reduced to substantially zero, then exposing the layer to an activating source of radiation whereby a latent conductivity pattern is formed in the radiation struck areas, followed by uniformly positive charging the layer whereby the radiation struck areas exhibiting the conductivity pattern dissipate the charge, while the areas unexposed to radiation retain a positive charge. A positive or negative image may be formed by developing either the positively charged areas or the latent conductivity pattern.

This invention relates to xerography, and more specifically to a system utilizing a zinc oxide photoconductor.

In the art of xerography as described in U.S. Pat. No. 2,297,691 to Carlson, a substantially conductive base having thereon a photoconductive insulating surface is electrostatically charged under dark room conditions. The charged photoconductive layer is then exposed to a source of activating radiation to form a light and shadow image. The charge on the plate leaks off rapidly to the base plate in proportion to the intensity of the light which strikes a given area. After such exposure, which forms a latent electrostatic image, the surface of the plate is then contacted with electroscopic marking particles under dark room conditions. The particles adhere to the areas where the electrostatic charges remain forming a powder image corresponding to the electrostatic image. This powder image may then be transferred to a sheet of transfer material resulting in a positive or negative print, as the case may be, having excellent detail and quality. If desired, the base plate may be made of relatively inexpensive material such as paper, and the powder fixed directly to the paper itself.

Initially, as disclosed by Carlson, suitable photoconductive insulating coatings comprised anthracene, sulfur, or various mixtures of these materials, and sulfur with selenium, etc. to thereby form uniform vitreous coatings on a base material. Subsequently, the discovery of the photoconductive insulating properties of highly purified vitreous selenium resulting in this material becoming the standard in commercial xerography.

The photoconductive speed of vitreous selenium is many times that of the prior art photoconductive insulating materials. Vitreous selenium, however, suffers from several defects. The first being that its spectral response is very largely limited to the blue or near ultraviolet, and second, the prepartion of the uniform films of vitreous selenium require highly involved and critical processes, particularly vacuum evaportaion. In addition, vitreous selenium by its nature requires a relatively firm and uniform support such as a metal base. This, along with the high cost of selenium, renders it somewhat impractical

for use as a disposable xerographic plate such as a paper base plate using vitreous selenium.

The development of zinc oxide for xerographic application has apparently met the need for an economical and highly satisfactory photoconductive member. U.S. Pats. Nos. 3,121,006 and 3,121,007 to Middleton et al.; 3,010,884, to Johnson et al.; 3,051,569 to Sugarman et al.; 3,052,539 to Greig; and 3,152,895 to Tinker et al., each disclose the use of zinc oxide in a disposable photoconductive member.

A typical electrostatic process involving zinc oxide, consists of coating the surface of a backing member such as paper with zinc oxide dispersed in an electrically insulating film forming vehicle such as a silicon resin. This photoconductive paper is then subjected to a high voltage corona discharge which produces an electrostatic charge on the surface of the paper. The paper is then exposed to a light and shadow image wherein the portions exposed to light rays are discharged leaving the remainder of the surface in a charged condition or with an electrostatic latent image on its surface. This image is then rendered visible by any suitable manner such as applying developer powder which adheres electroscopically to the charged areas of the sheet. The powder image thus formed may be fixed directly to the photoconductive coating, for example, by heating to fuse a thermoplastic resin incorporated in the powder.

The normally accepted mode of charging zinc oxide papers as known in the art, is by a negative potential. When "positive" corona charging is attempted it is generally unsatisfactory because the positive potential decays in times almost too short to measure. Thus, in conventional xerographic applications, zinc oxide photoconductive elements are charged to a negative potential by corona charging. The desirability of being able to charge zinc oxide photoconductors to a positive potential would allow for greater versatility and machine design, result in greater control in the ultimate reproduction properties of a system utilizing zinc oxide photoconductors, and afford an opportunity to use systems amendable to the combination of both negative and positive corona charging.

It is, therefore an object of this invention to provide a zinc oxide binder plate which overcomes the above noted disadvantages.

It is another object of this invention to provide a method of treating zinc oxide photoconductive members to be effectively used in a system utilizing positive charging.

It is yet another object of this invention to provide a method of positive charging zinc oxide photoconductors.

It is a further object of this invention to provide a system utilizing both positive and negative charging of zinc oxide photosensitive elements.

It is another object of this invention to provide an improved method of using zinc oxide photoconductors.

The foregoing objects and others are accomplished in accordance with this invention by exposing a conventional zinc oxide photosensitive element such as zinc oxide coated paper, binder plate, or the like, which has been "fatigue imaged" by exposure to a source of activating radiation such as light, to a source of positive potential, whereby a developable electrostatic image is thereby formed in the unfatigued areas. The fatigue image corresponds to the areas of the photosensitive zinc oxide which have been struck by light and are in the fatigued condition with the unilluminated areas being in a "relaxed" or equilibrium condition.

Before the zinc oxide photosensitive element is exposed to a source of activating radiation to form a fatigue image, or more correctly, a selective conductivity pattern, it must be first "relaxed" to prepare it for the subsequent

fatigue imaging step. By "relaxed," it is meant that the plate has come to an equilibrium or electrically neutral condition, i.e., substantially free from fatigue which is the persistent electrically conductive condition resulting from excitation of the photoconductor by light or heat. The zinc oxide photosensitive element or plate may be conveniently relaxed by storing under dark room conditions for an extended period of time such as for 24 hours. This storage results in a plate, which may have been previously fatigued, returning to its original relaxed condition which would render it sensitive to activating radiation. It has now been discovered that the plate may be relaxed immediately by exposing it to a source of negative potential. This method of relaxing has the advantage over storing under dark room conditions in that a relaxed plate is attained in a minimum amount of time and the zinc oxide plate is freer from fatigue or residual voltage than by storing under dark room conditions.

Once relaxed, the plate is then exposed to a source of activating radiation such as light in the form of the desired image. This activating radiation causes the exposed areas of the zinc oxide photoconductive layer to be selectively fatigued or rendered conductive while the unexposed areas remain free from fatigue or still in a neutral or relaxed state. The surface is then exposed to a source of positive potential which creates positive charges in the unexposed areas while the conductivity pattern in the fatigued areas dissipates the charge in image configuration. The surface now containing a latent electrostatic image is developed by any conventional means such as cascade, brush, aerosol, etc., to form a positive image of the original. If desired, the conductivity pattern can also be developed to form a negative of the original. Generally, the zinc oxide plates are uniformly charged to the appropriate negative and positive potentials and selectively exposed to activating radiation. If desired, however, the plates may be simply negative charged through a mask or stencil to form the desired image directly as a latent conductivity pattern, or as a "relaxed image" which is subsequently positively charged and developed.

When relaxed through the use of a negative potential, the surface may be neutralized by a subsequent positive potential followed by exposure, positive charging, and development. Alternatively, the negative potential may be used to relax the plate followed by exposure to light to form a fatigue image, followed by the application of a positive potential, and then development.

The range of negative voltage is not critical. Only that voltage necessary to relaxe the plate or eliminate fatigue is required. In using a Xerox Flat Plate Model D Scorotron as a charging unit, and subjecting a standard vitreous selenium plate containing a 50 micron layer of selenium on a conductive metallic backing to two passes through the charging area of the scorotron results in the selenium plate retaining a potential of about 600 volts negative or positive polarity. The polarity of the voltage depends upon the setting of the voltage control on the scorotron.

If a relaxed zinc oxide plate is used under the standard conditions defined above, the plate will retain a positive voltage of up to 100 volts and higher, depending upon the quality of the zinc oxide, and whether or not it has been treated with a sensitizer.

If a relaxed zinc oxide plate has been relaxed with negative charging by a number of passes through the Model D Scorotron, and it is desired to neutralize the negative charge prior to exposure to radiation to form a conductivity pattern, only a single pass through the scorotron under the positive polarity voltage setting is necessary to effectively neutralize the plate to a voltage of substantially zero.

It can be seen that through the use of applicant's novel method, images may be attained with the exposure source away from a charging unit. For example, a relaxed plate can be physically taken away from a charging unit, exposed to a source of light and shadow to form a fatigue image or conductivity pattern, and then returned to a positive charging unit to place a positive charge in the unexposed areas, followed by developing said charge to form a visible image.

Any conventionally used zinc oxide papers or plates such as those mentioned in the foregoing patents are included within the scope of this invention. The zinc oxides which are suitable are those which are substantially electrically nonconductive in the dark. When exposed to light, the zinc oxide should have a surface photoconductivity of a certain level in order to be of practical use of xerographic process. The zinc oxide may be prepared in a white form or in an orange-pink form commonly referred to as "pink form."

The zinc oxide is dispersed in an electrically insulating, film forming material which may be any one of a number of substances. Synthetic resinous materials having high dielectric constant and high dielectric strength are suitable. Typical resins are polyvinyl acetate, copolymers of vinyl chloride-vinyl acetate, polystyrene, and silicone resins. Other resin-like materials such as cellulose ethers and cellulose esters may also be used. Suitable examples of these types of materials are methyl or ethyl cellulose and cellulose nitrate. Natural resins are also suitable, shellac being but one example. In addition, other resinous materials are also suitable. Typical are various waxes such as paraffin, carnauba wax, and others. In ddition to being electrically insulating and film forming, the binder should also be water insoluble and should be sufficiently flexible when in the form of a thin film, to be practical as a coating for paper. Optionally, plasticizers for the resins above may be used to increase their flexibility.

Although a paper base may be preferred for disposable zinc oxide photoconductive elements, the photoconductive coating may be applied to a base which is electrically conductive, such as, for example, aluminum sheet, metal foil, or paper loaded with carbon black.

In order to broaden the spectral response of zinc oxide photoconductors, the oxide may be dyed with any suitable sensitizing dye which is capable of absorbing radiant energy and transferring the absorbed energy to the photoconductor. Among the typical sensitizing dyes which have been used with zinc oxide are: fluorescein, eosin, erythrosin, rose bengal, malachite green, crystal violet, basic fushian, methyl green, brilliant green, and many more.

The methods of manufacturing zinc oxide papers which are suitable for use in the method of this invention are adequately set forth by the patents mentioned above and are particularly shown by the patents to Greig and Sugarman et al.

Any suitable charging apparatus may be used for the method of this invention. Typical apparatus includes conventional corona charging devices such as that of Walkup shown in U.S. Pat. No. 2,777,957. Another typical apparatus is a Xerox Flat Plate Model D Scorotron available from Xerox Corporation of Rochester, N.Y.

The following examples using zinc oxide plates define the present invention with respect to a method of utilizing positive charging of zinc oxide. The parts and percentages in the disclosure are by weight unless otherwise indicated. The examples below are intended to illustrate the various preferred embodiments of this invention.

EXAMPLE I

A zinc oxide plate is prepared by making a mixture of one part by weight of zinc oxide (a pigment grade obtained from New Jersey Zinc Co. under the trade name Florence Green Seal No. 8) and two parts by weight of a binder consisting of the silicone resin 5071 available from Dow Corning. This mixture is thoroughly mixed by mechanical agitation to insure that the photoconductor is uniformly dispersed in the binder. The mixture is then spread over a 4 x 5 inch aluminum plate by means of a

draw rod and air dried to give a coating approximately 9 microns thick.

EXAMPLE II

The zinc oxide plate of Example I is fatigued by exposing to room light for a period of about 10 minutes. The fatigued plate is then positive charged with two passes in a Xerox Flat Plate Model D Scorotron charging unit available from Xerox Corporation of Rochester, N.Y. As measured with an electrometer after positive charging, the voltage on the plate is about +30 volts. The plate is again fatigued by exposing to room light for 10 minutes to obtain the residual potential. The residual potential is defined as a potential after exposure to room light subsequent to charging and is measured as 20 volts. This example demonstrates that a fatigued plate (fatiguing by exposing to room light) which is positive charged, attains only a 10 volt differential between the residual potential and the resultant positive potential.

EXAMPLE III

The zinc oxide plate of Example I is fatigued as in Example II with room light. The plate is then charged to a negative potential to relax the plate by two passes in the Xerox Model D Scorotron. The plate is then charged to a positive potential by two passes in the Model D Scorotron. Through the use of an electrometer, the positive voltage is recorded as +60 volts and the sheet again exposed to room light for 5 minutes to determine the residual potential which is 10 volts. It can be seen that through the use of a prior negative charging operation to relax, followed by a positive charging step, that a differential of 50 volts between the attained positive, voltage and the resulting residual voltage was attained. This is 40 volts more than that attained in Example I where no prior relaxing step (negative charging) is used in combination with the positive charging step.

EXAMPLE IV

The plate of Example I is negative relaxed and positive charged by the method of Example III and shows a positive charge voltage of 55 volts, and a resultant residual potential of 10 volts resulting in a differential of 45 volts.

EXAMPLE V

The plate of Example I is treated by the method of Example II and shows the charged voltage of +20 volts and a residual of +20 resulting in no voltage differential between the positive charge voltage and the residual.

EXAMPLE VI

The plate of Example IV is repeatedly charged by 10 passes under a positive potential setting of the Model D Scorotron in an attempt to give a maximum potential. The plate is still only able to retain a positive voltage of 20 volts, and upon exposure to room light for 10 minutes still shows a residual of 20 volts, resulting in no differential between the charged and residual voltage.

EXAMPLE VII

The zinc oxide plate of Example I is treated by the method of Example IV except that in positive charging, the paper is passed 10 times through the Model D Processor in order to give a maximum positive potential. The charged positive potential is 85 volts. After flooding with room light, a residual voltage of 15 volts is found. This is a differential of 60 volts.

EXAMPLE VIII

The zinc oxide plate of Example I is charged to a negative potential to relax by two passes through the Model D Scorotron. The plate is neutralized by a single pass through the Model D Scorotron at a positive potential. The plate is then exposed under dark room conditions to an image using a light exposure of about 250 foot-candle-seconds of white light. The paper is then positive

charged with 4 passes through the Model D Scorotron, and then developed by cascading with electroscopic marking particles. A sheet of paper is placed over the toned plate and positive charged by two passes in the Model D Scorotron, and then removed. The toner image is thereby transferred to the sheet of paper and made permanent by heat fusing. A good copy of the original is obtained by this method.

EXAMPLE IX

The zinc oxide plate of Example I is treated by the method of Example VIII except that after the initial negative charging, the plate is then exposed to an image without neutralizing the negative potential by positive charging. Following the exposure to form the image, the plate is then charged to a positive potential with 4 passes under the Model D Scorotron and then developed in the same manner as set forth in Example VIII. A good copy of the original is obtained.

EXAMPLE X

The zinc oxide plate of Example I is treated by the method of Example VIII except that the toner image is fused to the zinc oxide plate and not transferred. This method results in a good copy of the original.

EXAMPLE XI

The zinc oxide plate of Example I is treated by the imaging method of Example VIII, except for the elimination of the negative charging step and the neutralization step. The plate failed to hold an adequate charge, resulting in no image.

It can be seen from the above examples that the negative charging step prior to image results in a retained voltage sufficient to produce good images (Examples III, IV, VII, VIII, IX, and X). This is contrasted by low voltages and no image or very poor images obtained by the zinc oxide plate when the negative charging step is eliminated (Examples II, V, VI and XI).

EXAMPLE XII

A zinc oxide plate of the composition of Example I is prepared by the method of Example I except for the addition of Rose Bengal #2, a sensitizing dye, which is added to the mixture in the ratio of 1 gram of dye per 1000 grams of zinc oxide powder as a 1% solution in methyl alcohol.

EXAMPLE XIII

The zinc oxide plate of Example XII, sensitized with Rose Bengal #2, is fatigued by exposure to room light for 15 minutes. The sheet is then charged to a positive potential by two passes through the Model D Scorotron. The plate retains a charge of 70 volts. The plate is then fatigued by exposure to room light for 15 minutes, negative charged by two passes on a Model D processor followed by positive charging on a Model D processor for 2 passes. The voltage now observed, after the negative charging to relax, is 120 volts as opposed to only 70 volts without a prior negative charging step. The plate is again fatigued by exposure to room light for 15 minutes and then positive charged again 2 passes in a Model D processor. The voltage as measured with an electrometer is 60 volts. After flooding with room light to fatigue, the residual voltage is measured at 40 volts.

EXAMPLE XIV

The zinc oxide plate of Example XII is fatigued by exposure to room light for 10 minutes. The plate is then relaxed by charging to a negative potential by two passes through the Model D Scorotron under dark room conditions. The plate is then charged to a positive potential by two passes through the Model D Scorotron. The recorded voltage is 120 volts. The sheet is then exposed to room light for 10 minutes and shows a residual potential of 40 volts.

EXAMPLE XV

The zinc oxide plate of Example XII is fatigued by exposure to room light for 10 minutes and positive charged with 4 passes through the Model D Scorotron. The observed voltage is 75 volts. The plate is then exposed to room light and shows a residual potential of 55 volts.

EXAMPLE XVI

The zinc oxide plate of Example XII is fatigued by exposure to room light for 10 minutes. It is then charged to a negative potential by two passes through the Model D Scorotron to relax the plate. The plate is then positive charged by 4 passes through the Model D Scorotron. The recorded voltage as measured by an electrometer is 130 volts. The sheet is then fatigued by exposure to room light for 10 minues and the residual potential measured as 50 volts.

As seen by Examples I–XVI, through the use of a prior negative charging step, followed by a positive charging step, the voltage differential between the charged voltage and the residual after fatiguing, is measurably increased utilizing the prior negative charging step as opposed to simply attempting to positive charge a zinc oxide sheet without any prior treatment. Examples XII through XVI illustrate the same effect as shown by Examples I–XI only with increased voltages and differentials due to the fact that the oxide sheet used in Examples XII through XVI were sensitized with a dye. As shown by Example II, in particular, the fatigued sheet increased in potential from a residual of +20 volts to a charge voltage of 30 volts (a differential of only 10 volts) and has little sensitivity to light in that the residual potential is near that of the maximum potential attained after charging.

The advantages of the above described system are manifold. The application of positive charging in a zinc oxide system enables the use of a positive attractable toner, which was heretofore impossible due to the restrictions of negative charging. In addition, inasmuch as a fatigue or conductivity image has been formed by the light prior to positive charging, the image can be recharged a second time or as many times as desired to regenerate said image, a feature which is not available to conventional xerograpihc techniques. Also, in the negative charging mode, transferring of the electrostatic image followed by recharging and transferring of the electrostatic image repeatedly are not possible since the negative charging destroys the fatigue image. Another advantage exists in the fact that after negative charging to relax, the plate or unit containing the plate may be physically removed from the charging area and exposed at any time later without significant changes in the imaging characteristics of the plate. A further application of the above disclosed invention enables selective development of the portions of the zinc oxide sheet or plate at different times or even the addition of images over a previously formed image.

Although specific components and proportions have been stated in the above description of a preferred embodiment of this invention, other suitable materials and procedures such as those listed above, may be used with similar results. In addition, other materials and changes may be utilized which synergize, enhance or otherwise modify the plates.

Other modifications and ramifications of the present invention would appear to those skilled in the art upon reading the disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. A method of imaging which comprises:
   (a) relaxing a fatigued photosensitive element containing a photoconductive zinc oxide binder layer by uniformly exposing said surface to a source of negative potential,
   (b) bringing said surface to a substantially zero potential by exposing said element to a neutralizing source of positive potential,
   (c) exposing said surface to an activating source of radiation whereby a latent conductivity pattern is formed in the radiation struck areas, and
   (d) uniformly positive charging said surface whereby said radiation struck areas exhibiting a latent conductivity pattern dissipate the charge, while the areas unexposed to radiation retain a positive charge, and
   (e) developing said plate to form a visible image.

2. The method of claim 1 wherein the areas retaining the positive charge are developed.

3. The method of claim 1 wherein the conductivity pattern is developed immediately after step (c).

4. An imaging method which comprises:
   (a) relaxing a photosensitive element containing a photoconductive layer of zinc oxide in a binder by uniformly exposing the surface of said element to a source of negative potential,
   (b) exposing said surface to a source of activating radiation whereby a latent conductivity pattern is formed in the radiation struck areas, and
   (c) uniformly positive charging said surface whereby said radiation struck areas exhibiting a latent conductivity pattern dissipate the charge, while the areas unexposed to radiation retain a positive charge, and
   (d) developing said plate to form a visible image.

5. The method of claim 4 wherein the areas retaining the positive charge are developed.

6. The method of claim 4 wherein the conductivity pattern is developed immediately after step (b).

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CERTIFICATE OF CORRECTION

Patent No. 3,519,420 Dated July 7, 1970

Inventor(s) William L. Goffe

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

Column 1, line 8, delete "651,032" and insert --561,032--.

SIGNED AND
SEALED
OCT 13 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents