Sept. 4, 1962 H. G. GREIG 3,052,540

DYE SENSITIZATION OF ELECTROPHOTOGRAPHIC MATERIALS

Filed April 20, 1959 2 Sheets-Sheet 1

Fig. 1.

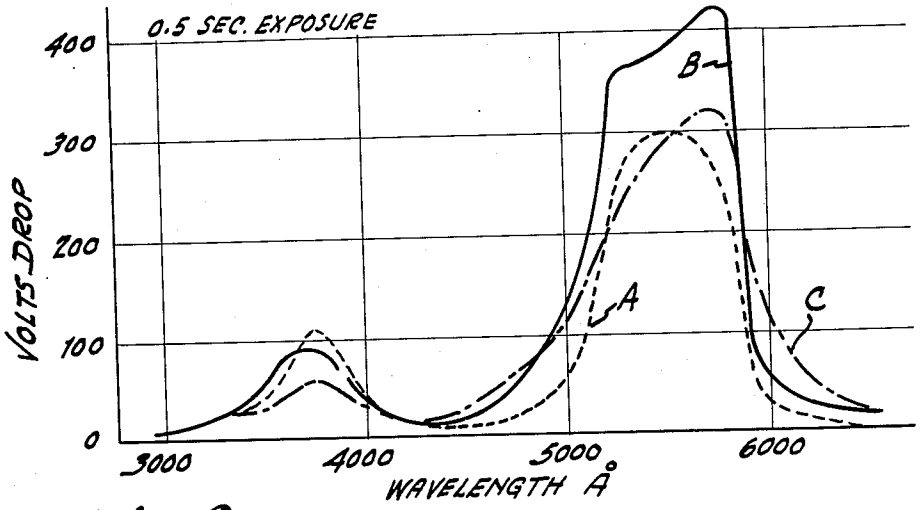
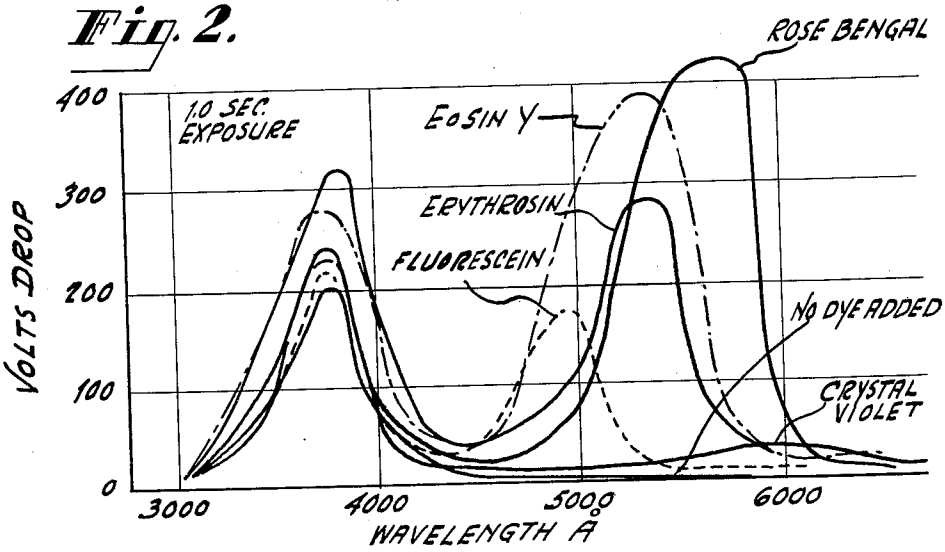


Fig. 2.



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Fig. 3.

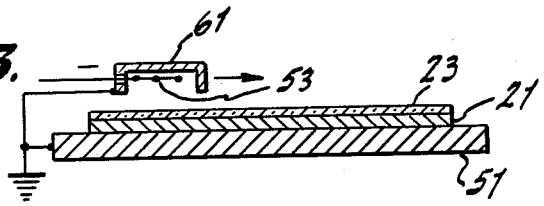


Fig. 4.

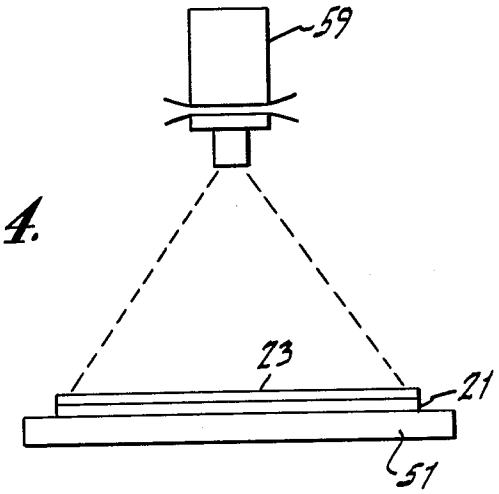
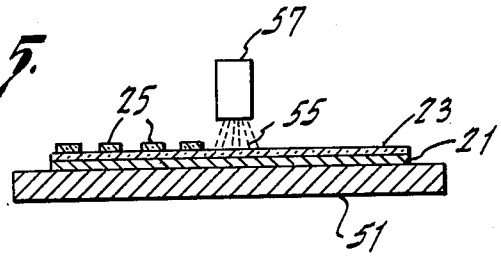


Fig. 5.



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DYE SENSITIZATION OF ELECTROPHOTOGRAPHIC MATERIALS

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Filed Apr. 20, 1959, Ser. No. 807,714
14 Claims. (Cl. 96—1)

This is a continuation-in-part of U.S. patent application Serial No. 433,898, filed June 2, 1954, and now abandoned, by H. G. Greig, the applicant herein, and assigned to the same assignee thereof.

This invention relates to photoconductive materials and devices particularly useful in electrostatic printing and to methods of making and using said photoconductive devices.

An electrostatic printing process is that type of process for producing a visible record, reproduction or copy which includes as an intermediate step, converting a light image or electrical signal into an electrostatic charge pattern on an electrically-insulating base. The process may also include the conversion of the charge pattern into a visible image which may be a substantially faithful reproduction of an original except that it may be a different size.

A typical electrostatic printing process may include coating a surface of a relatively conductive backing member with a photoconductive insulating material such as selenium, anthracene, or sulphur, and then providing an electrostatic charge on the surface of the photoconductive coating. A light image is focused on the charged surface, discharging the irradiated areas, while leaving the remainder of the surface in a charged condition, thereby forming an electrostatic image or pattern of electrostatic charges. The electrostatic image may be rendered visible by applying thereto developer powder particles which are held electrostatically to charged areas of the sheet. The powder image thus formed is transferred to another surface upon which the reproduced image is desired and then fixed thereon. A detailed description of the steps of such a process may be found in U.S. Patent 2,297,691, issued October 6, 1942, to C. F. Carlson.

An improved electrostatic printing process is described by H. G. Greig in U.S. patent application, Serial No. 383,677, filed October 1, 1953, and in C. J. Young and H. G. Greig, "Electrofax—Direct Electrophotographic Printing on Paper," RCA Review, volume 15, No. 4, pages 469 to 484 (December 1954). Greig's improved process eliminates the intermediate step of transferring the powder image and produces the powder image directly upon the desired surface. A recording element for his improved process comprises a backing sheet, such as paper, coated with specially-selected photoconductive white zinc oxide particles suspended in an electrically-insulating film-forming binder.

The photoconductive white zinc oxide-binder recording elements have been found to exhibit unusual and unexpected characteristics especially useful in electrostatic printing. The spectral response thereof peaks sharply in the near ultraviolet region of the spectrum with sensitivity extending into the blue end of the visible region of the spectrum. This spectral response characteristic is advantageous for many applications. However, in other

applications a broadened spectral response is desirable in order to more closely match the spectrum of the light image to which the recording element is exposed or to provide color separation of the light image.

It is an object of this invention to provide improved photoconductive materials and devices having an extended and predetermined spectral response especially useful as recording elements for electrostatic printing.

Another object is to provide improved methods of and means for extending the spectral response of photoconductive white zinc oxide-binder recording elements for electrostatic printing.

Another object is to provide methods of and means for adsorbing an optically sensitizing dye to photoconductive white zinc oxide particles in recording elements for electrostatic printing.

Another object is to provide improved methods of and means for electrostatic printing.

In general, the invention includes a photoconductive insulating material comprising finely-divided photoconductive white zinc oxide particles in an electrically-insulating, film-forming binder, and having incorporated therein an organic dye which is capable of absorbing radiant energy in a band of wave lengths to which said zinc oxide particles are substantially insensitive and transferring said adsorbed energy to said zinc oxide particles. A recording element for electrostatic printing may comprise a backing member having a surface coated with a photoconducting insulating material of the invention.

The photoconductive insulating materials herein are characterized by exhibiting the photoconductive spectral response of white zinc oxide-binder recording elements and also an additional photoconductive spectral response in the visible region of the spectrum. The additional spectral response is definite and predetermined, being a characteristic of the particular organic dye used to sensitize the recording element. Since many of the organic dyes used herein for extending the spectral response may be bleached easily and conveniently, it is possible to combine the advantages of wider spectral response with a white background where this is desirable.

The organic dye used herein for extending the spectral response of a recording element herein is adsorbed upon the surface of the zinc oxide particles. This adsorption may be achieved by staining the white zinc oxide particle with the dye before mixing with the binder, by adding the dye to the zinc oxide-binder coating dispersion before coating the mixture upon a support, or by staining the completed coating with the dye.

The invention includes also methods for using the recording elements herein in an electrostatic printing process. In order to remove the color of the dye, the dye may be bleached to a colorless material after the powder image has been formed. It has been found unexpectedly that one convenient method for bleaching is simply to expose the recording element to light which by itself, bleaches the dye in many of the recording elements herein.

The foregoing objects and other advantages are described in greater detail in the following description by reference to the accompanying drawings in which:

FIGURE 1 is a family of curves illustrating the effect of dye concentration upon the spectral sensitivity of a recording element of the invention;

FIGURE 2 is a family of curves illustrating the effect of different sensitizing dyes upon the spectral sensitivity of recording elements of the invention;

FIGURE 3 is a partially schematic sectional view of an apparatus for producing a blanket electrostatic charge upon the surface of a recording element of the invention;

FIGURE 4 is an elevational view of an apparatus for projecting an optical image upon the charged surface of the recording element of FIGURE 3; and

FIGURE 5 is a sectional view of an apparatus for developing an electrostatic image upon the recording element of FIGURE 4.

Similar reference characters are applied to similar elements throughout the drawing.

EXAMPLE 1

An improved electrophotographic recording element may be prepared by coating a paper backing member with a photoconductive insulating material of the invention. To prepare a preferred photoconductive insulating material, mix the following ingredients:

80 grams of a silicone resin solution (containing 60% solids), such as GE Silicone Resin SR–82, marketed by the General Electric Company, Pittsfield, Massachusetts,

106 grams of toluol, and

120 grams of photoconductive white zinc oxide—French Process Florence Green Seal pigment grade, marketed by the New Jersey Zinc Sales Company, Inc., New York, N.Y.

Prepare a solution of 0.04 gram of Rose Bengal dye dissolved in 5 cc. of methyl alcohol or other suitable solvent. This corresponds to about 0.033 weight percent dye with respect to the weight of zinc oxide. A suitable dye is Rose Bengal, C.I. No. 779 (First Edition), manufactured by the National Aniline Division, Allied Chemical and Dye Corp., New York, N.Y. This dye is also identified as C.I. 45400, C.I. Acid Red 94 (Second Edition), and as Tetraiodinate 4,5,7-tetrachloro fluorescein. This solution is added slowly to the zinc oxide mix with constant stirring. The mix is then ball-milled in a porcelain mill with porcelain balls for about three hours to insure complete mixing of the ingredients and to obtain a smooth, uniform consistency for the subsequent coating step.

The milled mix is then coated upon a sheet of paper and dried to remove the solvent. The dried coating layer is about .0001 to .0015 inch thick but preferably about .0005 inch thick for most applications.

In FIGURE 1, curve B represents the relative spectral response of the recording element of Example 1. Curve A illustrates the spectral response of a similar recording element containing about half the amount of dye (about 0.0167 weight percent) contained in the element of curve B. Curve C illustrates the spectral response for a similar recording element containing about twice the amount of dye (about 0.067 weight percent) contained in the element of curve B. It will be noted that the curves peak at about 3750 A. and between 5250 and 5750 A. When no dye is added, the curve has only one peak at about 3750 A.

FIGURE 2 shows a set of comparative curves wherein the dye (Rose Bengal) of Example 1 is replaced with other dyes such as eosin Y, fluorescein, erythrosin and crystal violet. When no dye is added, the element exhibits a single peak at about 3750 A. Where a dye has been incorporated, each element exhibits two peaks, one at about 3750 A. and one in another area of the spectrum and generally adding sensitivity in a band of wavelengths to which zinc oxide particles are substantially insensitive.

The curves of FIGURES 1 and 2 are obtained in the following manner. A recording element is prepared according to Example 1. The surface of the coating is then electrostatically charged to 600 volts, for example with a corona discharge apparatus. Incremental areas of the surface are exposed to light of a very narrow band of wavelengths. A standard Bausch and Lomb monochrometer having a tungsten lamp light source may be used to obtain the desired band of wavelengths. The curves of FIGURE 1 were obtained with a 0.5 second exposure and the curves of FIGURE 2 were obtained with a 1.0 second exposure. The voltage of the surface of the coating with respect to ground is measured before and after the exposure by means of a vibrating probe electrometer. The curves of FIGURES 1 and 2 represent a compilation of the voltage drops obtained by exposure to the respective wavelength bands for each combination of dye and zinc oxide-resin mix.

While a specific example of a recording element has been given, other materials and structures may be used. The backing member may be either a relatively insulating material such as paper, or it may be a relatively conducting material, such as metal foil or sheet, or paper loaded with carbon black.

In the research work to develop the electrophotographic recording elements described in patent application Serial No. 383,677, op. cit., it was noted that many white zinc oxides tested produced recording elements which did not print or printed very poorly. These white zinc oxides are referred to as semiconductive white zinc oxides. Most of these semiconductive white zinc oxides were made by the American process directly from zinc ore. Measurements of the equivalent voltage of the surface immediately after electrostatic charging in the dark indicated little or no retention of surface electrostatic charge. This is believed to be due to the rapid decay of electrostatic charge on coatings made with the semiconductive zinc oxides.

The remaining white zinc oxides, referred to as photoconductive white zinc oxides, produce coatings which retain sufficient electrostatic charge after electrostatic charging and may be used in the recording elements herein for electrostatic printing processes.

By special test disclosed in patent application Serial No. 383,677, op. cit., the semiconductive and photoconductive white zinc oxides may be distinguished by value of surface photoconductivity. The photoconducting white zinc oxides all have a value of surface photoconductivity higher than 10^{-9} ohms^{-1}/square/watt/cm.^{2}; whereas the semiconducting white zinc oxides all have values below this value.

The electrically-insulating, film-forming binder (also referred to as "vehicle") may be selected from a large group of substances. It is desirable for the binder to have a relatively high dielectric strength. These materials may be natural or synthetic resins or waxes. Examples of suitable resins are the vinyl resins, silicone resins, phenol formaldehyde compounds and cellulose ethers and cellulose esters. Shellac is an example of a suitable natural resin. Examples of suitable waxes are paraffin, carnauba wax and beeswax. Mixtures of two or more binders may be used. Plasticizers or similar modifying agents may be incorporated with the film-forming binder provided they do not adversely affect the electrical properties of the material.

The following dyes in the Table of Dyes, representing several different dye classes, are examples of dyes which sensitize the photoconductive white zinc oxide-binder recording element of Example 1. By "sensitize" is meant capable of absorbing radiant energy in a band of wavelengths to which zinc oxide particles are substantially insensitive and transferring said absorbed energy to the photoconductive white zinc oxide particles to produce a change in the conductivity of said zinc oxide particles. In each case, the recording element exhibits a peak at about 3750 A. in the original range of the white zinc oxide. However, in each case the recording element exhibits an additional peak over a narrower or wider range

at some other place on the spectrum. C.I. denotes Color Index number (Second Edition, 1957).

Table of Dyes

	C.I.=Color Index No. (2nd Ed., 1957)
I. Xanthene Dyes:	
Fluorescein	45350 (C.I. Acid Yellow 73).
Eosine	45380 (C.I. Acid Red 87).
Phloxine	45405 (C.I. Acid Red 98).
Phloxine B	45410 (C.I. Acid Red 92).
Erythrosine	45430 (C.I. Acid Red 51).
Rose Bengal	45440 (C.I. Acid Red 94).
II. Triarylmethane Dyes:	
Malachite Green	42000 (C.I. Basic Green 4).
Crystal Violet	42555 (C.I. Basic Violet 3).
Basic Fuchsine	42510 (C.I. Basic Violet 14).
Methyl Green	42590.
Brilliant Green	42040 (C.I. Basic Green 1).
Patent Blue	42045 (C.I. Acid Blue 1).
Brilliant Blue FCF	42090 (C.I. Acid Blue 9).
III. Thiazole Dyes:	
Thioflavine TG	49005 (C.I. Basic Yellow 1).
IV. Thiazine Dyes:	
Methylene Green	52020 (C.I. Basic Green 5).
Methylene Blue	52015 (C.I. Basic Blue 9).
V. Azine Dyes:	
Neutral Red	50040 (C.I. Basic Red 5).
Safranine Y	50240 (C.I. Basic Red 2).
Methylene Violet	50205 (C.I. Basic Violet 5).
VI. Acridine Dyes:	
Acridine Orange	46005 (C.I. Basic Orange 14).
VII. Diphenylmethane Dyes:	
Auramine O	41000 (C.I. Basic Yellow 2).
VIII. Cyanine Dyes:	
Ethyl Red	(Absorption Max. in alcohol 5602 A.)
Kryptocyanine	(1,1'-diethyl-4,4'-carbocyanine iodide.)
Pinacyanol	
Thiazole Purple	(3,3'-diethylthia carbocyanine iodide.)
IX. Mixture of Dyes:	
Methylene Grey	50431 (C.I. Basic Black 1).
X. Anthraquinone Dyes:	
Alizarine Red	58005 (C.I. Mordant Red 3).
Quinizarin	58050 (C.I. Pigment Violet 12).
Carbanthrene Yellow G (Flavanthrone)	70600 (C.I. Vat Yellow 1).

In the following examples, the dye mixtures are added to a base coating mix as previously described. The base coating mix with dye added is then dispersed by conventional methods (ball mill, roller mill, paint mill, colloid mill, etc.) as in Example 1. A suitable coating mix is,

80 grams silicone resin solution SR–82 (60% solids in xylene—mfg. G.E.)
106 grams toluene
120 grams zinc oxide, Florence Green Seal-8 (mfg. New Jersey Zinc Co.)

EXAMPLE 2

The addition of the following dye mixture to the base coating mix produces recording elements having a panchromatic response balanced for approximately equal sensitivity to blue, green and red light from a 100 watt incandescent lamp.

0.012 gram Fluorescein (sodium salt)
.005 gram Rose Bengal (potassium salt 88%)
.020 gram Brilliant Green (nat. aniline 93%)
5 ml. methanol

The finished coating is slightly off white in color. For increased sensitivity with a darker (gray-green color) colored coating the dyes can be increased in ratio.

EXAMPLE 3

The addition of the following dye mixture to the base coating mix produces recording elements having a panchromatic response but with widely different sensitivities to red, green and blue light for exposure to a 100 watt incandescent lamp as the light source.

0.0063 gram Patent Blue, C.I. 42045
.0025 gram Rose Bengal (88%), C.I. 45440
5 ml. methanol

The finished coating is slightly off-white having a greenish cast. Here again the overall sensitivity can be increased by increasing the dyes in ratio.

EXAMPLE 4

The addition of the following dye mixture to the base coating mix produces recording elements having a panchromatic response wherein the red and green sensitivity are about equal, with blue much lower using 100 watt incandescent lamp as the light source.

0.005 gram Rose Bengal (88%), C.I. 45440
.020 gram Brilliant Green, C.I. 42040
.040 gram Thioflavin TG, C.I. 49005
5 ml. methanol

The finished coating has a slightly greenish cast.

EXAMPLE 5

The addition of the following dye mixture to the base coating mix produces recording elements having a panchromatic response with slightly higher sensitivity to red and blue light than it does to the green light from a 100 watt incandescent lamp.

0.015 gram Fluorescein (sod. salt), C.I. 45350
0.015 gram Patent Blue, C.I. 42045
5 ml. methanol

The finished coating has a slightly gray-green cast.

EXAMPLE 6

The addition of the following dye mixture to the base coating mix produces recording elements having a panchromatic response but exhibiting widely different sensitivities to the red, green and blue light from a 100 watt incandescent lamp.

0.060 gram Brilliant Blue FCF (C.I. 42090)
0.036 gram Rose Bengal (C.I. 45440)
5 ml. methanol

The dried coating has a blue color.

EXAMPLE 7

The addition of the following dye mixture to the base coating mix produces a light gray coating that exhibits a well balanced response to the red, green and blue light from a 100 watt incandescent lamp.

0.020 gram Rose Bengal (C.I. 45440)
.010 gram Fluorescein (sod. salt) (C.I. 45350)
.015 gram Auramine O (C.I. 41000)
.005 gram Thioflavin TG (C.I. 49005)
5 ml. methanol

Up to about 0.5% by weight of dye with respect to the weight of zinc oxide may be incorporated. However, it is preferred to incorporate the minimum amount of dye capable of producing the desired result. Mixtures of dyes may also be used, for example methylene gray, or mixtures of other dyes if they are compatible. The above-mentioned dyes are the commercially obtainable dyes listed according to their commercial names. Each of these dyes is chemically defined according to its name and C.I. No. (Second Edition). The dyes as supplied may contain more or less amounts of inert ingredients according to the process by which they are made.

The sensitizing dye is believed to be adsorbed on the surfaces of the photoconductive white zinc oxide particles. Radiant energy to which the zinc oxide particles are substantially insensitive incident upon the zinc oxide-binder layer is absorbed by adsorbed dye molecules. The absorbed energy with more or less efficiency is then transferred to the zinc oxide particle increasing the electrical conductivity thereof.

The recording elements herein therefore exhibit the normal photoconductive spectral response of white zinc oxide-binder recording elements and also an additional photoconductive spectral response in the visible region of the spectrum. It may be stated that the dye broadens the light absorption band of the zinc oxide. This spectral response is predetermined by the selection of the particular sensitizing dye. The energy transfer is not

believed to be thermal because the spectral sensitivity due to the dye is orders of magnitude faster and more efficient than thermal processes.

The sensitizing effect of a dye upon photoconductive white zinc oxide depends on several factors. Some important factors are (1) the amount of light absorbed by the dye, (2) the absorption characteristics of the dye in the light spectrum, and (3) the efficiency of the transfer of energy absorbed to the photosensitive zinc oxide-binder element will play a part. Two dyes may have very similar light absorption characteristics and one be a poor sensitizer while the other with better energy transfer be a good sensitizer. Some dyes have no appreciable sensitizing action for the zinc oxide-binder element at all.

The coating mix of Example 1 may be prepared in several ways. The simplest method is to dissolve the film-forming material in an organic solvent capable of effecting solution and then dispersing the other ingredients therein. Alternatively, the ingredients may be dry-blended by kneading with a film-forming binder added at a sufficiently high temperature to render it plastic. In the case of waxes, the ingredients may be mixed together in the molten wax.

The proportion of photoconductive white zinc oxide to electrically-insulating, film-forming binder in the finished coating may be varied. The preferred ranges are 50 to 90% of zinc oxide and 50 to 10% of film-forming binder. The optimum proportions are dependent upon the nature of the photoconductor, the film-forming binder, the dye and the results desired.

EXAMPLE 8

An improved electrophotographic recording element may also be prepared by first dyeing the photoconductive white zinc oxide and then incorporating the dyed zinc oxide into the coating mix. For example: prepare a dye solution comprising 0.04 gram of fluorescein dissolved in 4 cc. of methyl alcohol. Stir this solution into a slurry comprising 120 grams of photoconductive white zinc oxide and 190 cc. of methyl alcohol until a uniform mixture is obtained. The dyed zinc oxide is filtered off and dried. A coating mix comprising 120 grams of dyed zinc oxide, 80 grams of a 60% silicone resin solution and 106 grams of toluol is ball-milled and coated on a sheet of paper as in Example 1. The materials of this example may be the same materials as in Example 1 with the exception of the dye.

EXAMPLE 9

An improved electrophotographic recording element may also be prepared by first coating a backing member with a zinc oxide-binder mix and then dyeing the coating with a suitable dye. For example, prepare a recording element according to Example 1 except exclude the dye. Prepare a dye solution comprising 0.05 gram of erythrosin in 200 cc. of ethyl alcohol. Moisten the surface of the zinc oxide-binder coating of the recording element with the dye solution. For example, immerse the coating in the solution or apply a swab of cotton moistened with the dye solution. The recording element is dried and is ready for use.

The recording elements of the invention may be utilized to receive a visible image thereon. For example, referring to FIGURE 3, the recording element of Example 1 is placed with its coated surface **23** facing upwards and its backing member **21** against a metal ground plate **51**. An electrostatic charging device **61** is passed, in darkness, over the photoconductive coating **23** to provide an over-all electrostatic charge thereon. The charging device **61** may comprise an array of fine wires **53** mounted near the grounded metal plate **51**. A source of D.-C. high voltage is connected between the wires **53** and the ground plate **51** to provide a negative potential of about —6000 volts on the wires with respect to the ground plate. The voltage is not critical but should be sufficiently high to cause a corona discharge adjacent the wires **53**. The surface of the coating **23** of the recording element passing under the charging device **61** becomes charged negatively. The apparatus and process may produce a blanket positive charge if the polarly of the wires **53** is positive with respect to the ground plate **51**.

The next step in the process is to discharge selected areas of the charged surface of the recording element in order to produce an electrostatic image thereon. Referring to FIGURE 4, this may be accomplished by exposing the recording element to a light image derived, for example, from a projector **59** containing the printed matter to be reproduced. The light image is focused on the charged surface of the coating **23**. The object to be printed may, however, be any object used in ordinary photographic processes. Wherever the light strikes the surface of the coating **23**, the electrostatic charge thereon is reduced or removed. This leaves an electrostatic image or pattern of electrostatic charges corresponding to the dark portions of the light image. Other methods of producing an electrostatic image may also be used.

The electrostatic image may be stored for a time in darkness if desired. Ordinarily the next step is to develop the electrostatic image. Referring to FIGURE 5, development may be accomplished by maintaining the recording element in darkness and passing a developer brush **55** containing a developer powder (toner) across the surface of the coating **23** bearing the electrostatic image. The developer brush comprises a mixture of magnetic carrier particles, for example, powdered iron and developer powder particles (toner particles). The mixture is secured in a magnetic field by a magnet **57** to form a developer brush. This method of development is more completely described by H. G. Greig in U.S. Patent No. 2,874,063, issued February 17, 1959. The powder image, produced by the development of the electrostatic image, may be fixed directly to the recording element or may be transferred to another surface and fixed thereon. Other methods of development and fixing well known in the electrostatic printing art may be used.

If the colored background of the recording element due to the dye sensitization according to the invention is objectionable, the dye may be bleached after the image is developed. One convenient process for bleaching is by exposure to light. For example, kryptocyanine and pinacyanole are bleached by exposure to visible light in less than a minute.

The rate of bleaching by light depends upon the dye concentration, the intensity and spectral range of illumination and the nature of the dye. Most of the dyes enumerated herein may be bleached by exposure to light. Bleaching by exposure to light may be accomplished in a fraction of a second for some dyes under special circumstances. The incorporated dyes may also be bleached by chemical action by methods known in the chemical art.

Dye sensitization of the photoconductive white zinc oxide-binder electrophotographic elements herein are useful in both black-and-white and in color printing. The utility can be quite different from that normally achieved in silver halide photographic elements.

For example, one may provide a recording element sensitized with a mixture of dyes so it has a panchromatic response but with widely different sensitivities to different spectral bands in the visible light range. See examples above. A recording element of this character can be used to print different colors from a single color transparency by developing the images with non-overprinting toners and by using only a change in exposure time to go from one color to another in a repeat printing procedure. If for example the sensitivity is highest to red light, lower to yellow-green light and lowest to blue light, then with an incandescent light source, an exposure sufficient to discharge the image in the yellow-green areas will also discharge the white and red areas and only the blue image

will retain a charge. If this image is developed with a toner that will not retain a charge (a non-overprinting toner) then in a repeat printing procedure with exposure time reduced to just clear the red image areas, only the yellow-green areas will retain a charge. The white areas which receive the most light will be discharged with the red and the previously developed blue image will not retain a charge. In a like manner, the exposure time can be reduced further to just clear the white areas and the red image can be printed. If this is the last step any toner can be used to develop the image. This has no counterpart in silver halide photography.

One may balance a mixture of dyes to sensitize the photoconductive white zinc oxide-binder element so that it can have very nearly equal response panchromatically to light from a given light source. Such an element is useful not only for black-and-white printing but also for color printing from color transparencies and from opaque color prints by reflection optics. In color printing, filters are used to mask the light in the band where it is desired to print. A repeat charge and exposure is of course needed for each color. With dye sensitization a considerable increase in sensitivity is gained when a wide band emission light source, such as an incandescent lamp, is used.

Printing by reflection optics, especially from a subject having several different colors where the reflection of ultraviolet light from a background and a colored image may be very nearly the same, is made possible by the dye sensitization herein. The spectral response of the photosensitive element can be made to approximate the response of the human eye in the visible spectrum so that even a black-and-white print from a colored subject can show the color intensities in the proper relationship.

By the dye sensitization herein, one may match the light from a mono-chromatic or a narrow emission band light source such as a cathode ray tube. If such light is entirely in the visible range, the white zinc oxide-binder recording element without dye sensitization would be substantially insensitive. For example, fluorescein may be used in a recording element herein to sensitize for the light from a P11 phosphor in a CR tube.

What is claimed is:

1. A recording element for electrostatic photographic printing characterized by exhibiting the photoconductive spectral response of photoconductive white zinc oxide-binder recording elements and also an additional photoconductive spectral response in the visible region of the spectrum, said recording element including a photoconductive insulating layer consisting essentially of finely-divided photoconductive white zinc oxide particles in an electrically-insulating, film-forming binder and up to about 0.5% by weight with respect to the weight of said zinc oxide particles of at least one optically sensitizing dye which extends the photoconductive spectral sensitivity of said zinc oxide in the visible region of the spectrum, said zinc oxide particles constituting 50% to 90% by weight of said layer and said binder constituting substantially all of the balance of said layer.

2. A recording element for electrostatic photographic printing comprising a backing member carrying a photoconductive insulating layer about 0.0001 to 0.0015 inch thick consisting essentially of finely-divided photoconductive white zinc oxide particles dispersed in an electrically-insulating, film-forming binder and up to about 0.5% by weight with respect to the weight of said zinc oxide particles of at least one optically sensitizing dye which extends the photoconductive spectral sensitivity of said zinc oxide in the visible region of the spectrum, said zinc oxide particles constituting 50% to 90% by weight of said layer and said binder constituting substantially all of the balance of said layer.

3. A recording element for electrostatic photographic printing comprising a backing member having a surface coated with a mixture consisting essentially of finely-divided photoconductive white zinc oxide particles dispersed in an electrically-insulating, film-forming binder and up to about 0.5% by weight with respect to the weight of said zinc oxide particles of at least one optically sensitizing dye which extends the photoconductive sensitivity of said zinc oxide in the visible region of the spectrum, said zinc oxide particles constituting 50% to 90% by weight of said mixture and said binder constituting substantially all of the balance of said mixture.

4. A recording element for electrostatic photographic printing comprising a backing member carrying a layer consisting essentially of finely-divided photoconductive white zinc oxide particles dispersed in an electrically-insulating, film-forming binder, said zinc oxide particles having adsorbed thereto up to about 0.5% by weight with respect to the weight of said zinc oxide particles of at least one optically sensitizing dye which extends the photoconductive spectral sensitivity of said zinc oxide in the visible region of the spectrum and selected from the group consisting of fluorescein, eosin, phloxine, phloxine B, erythrosin, rose bengal, malachite green, crystal violet, basic fuchsin, methyl green, brilliant green, patent blue, brilliant blue FCF, thioflavine TG, methylene green, neutral red, safranine Y, methylene violet, auramine O, ethyl red, thiazole purple, kryptocyanine, pinacyanole, methylene blue, ecridine orange, methylene gray, alizarin red S, carbanthrene yellow G, and quinizarin, said zinc oxide particles constituting 50% to 90% by weight of said layer and said binder constituting substantially all of the balance of said layer.

5. The recording element of claim 4 wherein said dye is rose bengal.

6. The recording element of claim 4 wherein said dye is erythrosin.

7. The recording element of claim 4 wherein said dye is fluorescein.

8. The recording element of claim 4 wherein a plurality of dyes are adsorbed on said zinc oxide particles.

9. The recording element of claim 4 wherein a combination of fluorecein, rose bengal and brilliant green are adsorbed on said zinc oxide particles.

10. The recording element of claim 4 wherein a combination of rose bengal, fluorescein, auramine O and thioflavin TG are adsorbed on said zinc oxide particles.

11. A recording element for electrostatic photographic printing characterized by exhibiting the photoconductive spectral response of photoconductive white zinc oxide and also an additional photoconductive spectral response in the visible region of the spectrum, said element comprising a paper backing member carrying a layer about 0.0001 to 0.0015" thick and having a composition consisting essentially of finely-divided photoconductive white zinc oxide particles in an electrically-insulating silicone resin binder and up to 0.5 weight percent with respect to the weight of said zinc oxide of an optically sensitizing dye which extends the photoconductive spectral sensitivity of said zinc oxide in the visible region of the spectrum, said zinc oxide particles constituting 50% to 90% by weight of said layer and said binder constituting substantially all of the balance of said layer.

12. A recording element for electrostatic photographic printing characterized by exhibiting the photoconductive spectral response of photoconductive white zinc oxide and also an additional photoconductive spectral response in the visible region of the spectrum, said element consisting essentially of a paper backing member carrying a layer about 0.0001 to 0.0015" thick and having a composition consisting essentially of finely-divided photoconductive white zinc oxide particles in an electrically-insulating silicone resin binder and up to 0.5 weight percent with respect to the weight of said zinc oxide of rose bengal, said zinc oxide particles constituting 50% to 90% by weight of said layer and said binder constituting substantially all of the balance of said layer.

13. A recording element for electrostatic photographic

printing characterized by exhibiting the photoconductive spectral response of photoconductive white zinc oxide and also an additional photoconductive spectral response in the visible region of the spectrum, said element consisting essentially of a paper backing member carrying a layer about 0.0001 to 0.0015" thick and having a composition consisting essentialy of finely-divided photoconductive white zinc oxide particles in an electrically-insulating silicone resin binder and up to 0.5 weight percent with respect to the weight of said zinc oxide of fluorescein, said zinc oxide particles constituting 50% to 90% by weight of said layer and said binder constituting substantially all of the balance of said layer.

14. A recording element for electrostatic photographic printing characterized by exhibiting the photoconductive spectral response of photoconductive white zinc oxide and also an additional photoconductive spectral response in the visible region of the spectrum, said element consisting essentially of a paper backing member carrying a layer about 0.0001 to 0.0015" thick and having a composition consisting essentially of finely-divided photoconductive white zinc oxide particles in an electrically-insulating silicone resin binder and up to 0.5 weight percent with respect to the weight of said zinc oxide of erythrosin, said zinc oxide particles constituting 50% to 90% by weight of said layer and said binder constituting substantially all of the balance of said layer.

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