United States Patent

[11] 3,619,154

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[21] Appl. No. **748,772**
[22] Filed **July 30, 1968**
[45] Patented **Nov. 9, 1971**

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[54] **INFRARED SENSITIZATION OF PHOTOCONDUCTIVE COMPOSITIONS EMPLOYING CYANINE DYES**
11 Claims, 3 Drawing Figs.

[52] **U.S. Cl.** ..... **96/1.7 R,** 96/130 R, 260/240.5 R
[51] **Int. Cl.** **G03g 5/00,** G03c 1/08
[50] **Field of Search** 96/1.5, 1.7, 1.8; 260/240.5

[56] **References Cited**

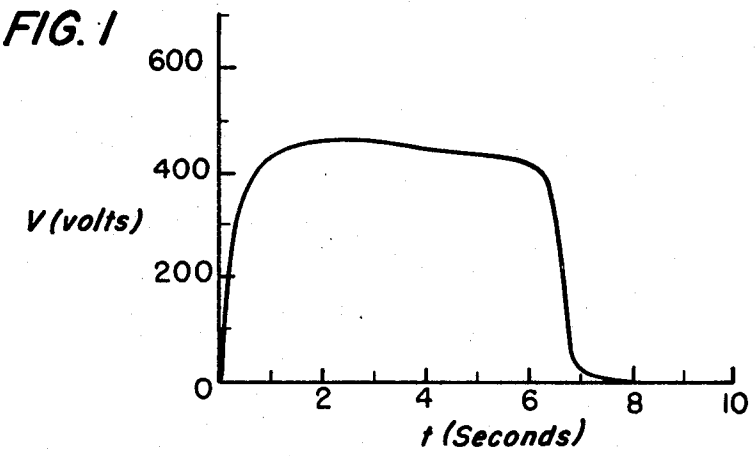
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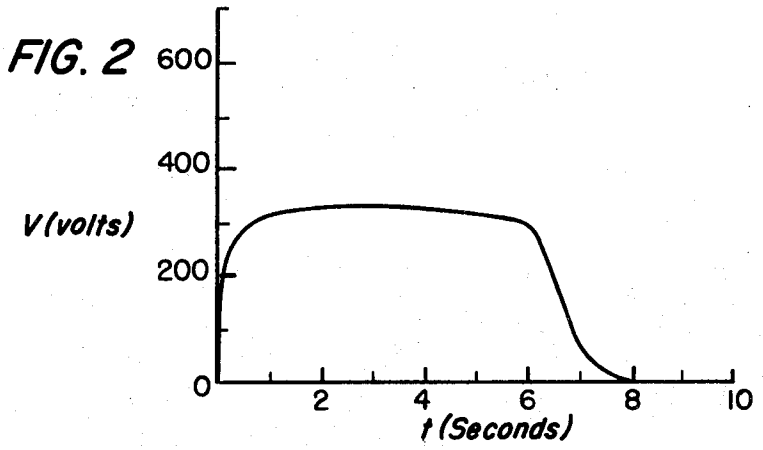
ABSTRACT: Photoconductive compositions comprising zinc oxide are sensitized in the near infrared region of the spectrum by near infrared-sensitizing cyanine dyes. The dyes adsorb onto the surface of zinc oxide and render it photosensitive to wavelengths of light above 700 millimicrons.

FIG. 1



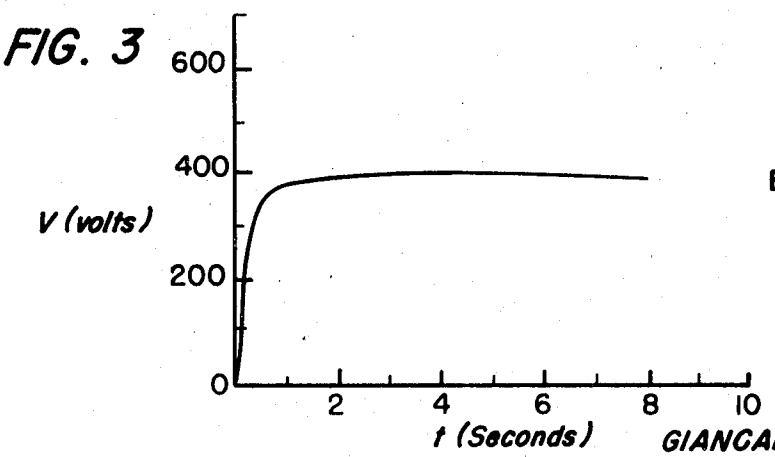
IR-1

FIG. 2



IR-2

FIG. 3



Bromophenol Blue

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INFRARED SENSITIZATION OF PHOTOCONDUCTIVE COMPOSITIONS EMPLOYING CYANINE DYES

BRIEF SUMMARY OF THE INVENTION

This invention relates to photoconductive compositions and more particularly to photoconductive compositions comprising zinc oxide having absorbed on the surface thereof a near infrared-sensitizing cyanine dye.

It is known that zinc oxide can be employed in making photoconductive layers on ordinary paper and that photographic copies can be prepared from these photoconductive papers. In one process, the zinc oxide layer is exposed to a photographic image, and a latent image is formed on the zinc oxide which can be developed into a photographic copy. In another process, the developed image is transferred from the zinc oxide sheet to a receiving sheet to make a photographic copy.

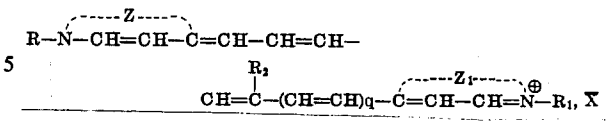
Zinc oxide normally has a spectral response in the ultraviolet region of the spectrum, at about 386 millimicrons. For an electrophotographic process, zinc oxide is generally sensitized to be responsive in the visible region of the spectrum at a wavelength between about 500 to 620 millimicrons, by the addition of low concentrations of dyes. Cyanine dyes are known in this connection as shown in U.S. Pat. No. 3,128,179. However, while the dyes there disclosed are satisfactory for sensitization of zinc oxide in the visible region, they do not provide sensitization above 700 millimicrons, the infrared region of the spectrum.

As is known, photoconductive layers comprising zinc oxide are generally placed on a paper support which when grounded is given a negative electrostatic charge on the zinc oxide layer, usually by means of ion transfer from a corona discharge. When the photoconductive layer is exposed to a photographic image, the unexposed portions of the zinc oxide layer retain their negative electrostatic charge while the exposed portions of the photoconductive layer, which receive visible or ultraviolet radiation, lose some or all of their negative electrostatic charge. The resulting latent image represented by the unexposed portions of the photoconductive layer can be developed by use of a toner powder which has an electrostatic charge opposite to the negatively charged unexposed portions of the photoconductive layer. The toner powder is thus attracted to the unexposed portions and is affixed thereto by melting the resin contained in the toner powder so that the toner particles fuse to the surface of the photoconductive layer to provide a permanent copy.

In the past, the zinc oxide layer has been exposed in a copy machine, such as the SCM Electrostatic Copier, which uses a tungsten lamp for the exposure. We have found that while the conventional zinc oxide sheet is sensitized with dyes to be responsive in the visible region of the spectrum, about 80 percent of the light emitted from a tungsten lamp is in the near infrared, the spectral region above about 700 millimicrons. It can be seen, therefore, that the electrophotographic process can be made more efficient by sensitizing zinc oxide in the near infrared region of the spectrum. Further, we have found that the intensity of the exposing source can be greatly reduced and excellent prints obtained when zinc oxide is sensitized in the near infrared region of the spectrum. Under the same conditions of low intensity, a standard zinc oxide photoconductive layer, sensitized in the known manner in the visible region of the spectrum, will not yield a print.

By use of near infrared-sensitizing dyes for zinc oxide, another problem with present zinc oxide papers can be overcome. Even though the presently known dyes for sensitizing zinc oxide in the visible region of the spectrum are used in low concentrations, the dyes in many instances impart an undesirable color to the zinc oxide coated papers. For example, uranine and Rose Bengal impart a pink color to the zinc oxide electrophotographic layer, and bromophenol blue tends to impart a purple color. With the use of an infrared-sensitizing dye, the electrophotographic layer absorbs little, if any, light in the visible region of the spectrum. The result is that the infrared-sensitizing dye does not tend to color the zinc oxide layer, and the final product appears whiter and has a higher luminosity.

The types of dyes which can be used in practicing our invention comprise those dyes which can sensitize zinc oxide in the near infrared region of the spectrum, i.e., between 700 and 2,000 millimicrons. In particular, we have found that cyanine or polymethine dyes having at least a seven carbon chain (heptamethine structure) bridging two heterocyclic nuclei are quite useful in practicing the present invention. In general, these dyes can be represented by the following general formula:



wherein R and R_1 each represents a member selected from the group consisting of an alkyl group (e.g., methyl, ethyl, propyl, etc.), a hydroxyalkyl group (e.g., hydroxyethyl, hydroxypropyl, etc.), an alkoxyalkyl group (e.g., β-methoxyethyl, β-ethoxyethyl, etc.), a carboxyalkyl group (e.g., carboxymethyl, β-carboxyethyl, etc.), a carbalkoxyalkyl group (e.g., carbomethoxymethyl, β-carbomethoxyethyl, etc.), an acyloxyalkyl group (e.g., β-acetoxyethyl, γ-acetoxypropyl, etc.), and an aralkyl group (e.g., benzyl, β-phenethyl, etc.); R_2 represents a hydrogen atom, an alkyl group, an aryl group (e.g., phenyl, hydroxyphenyl, etc.), or an acetoxy group; q represents a positive integer from 1 to 3; X represents an acid anion (e.g., chloride, iodide, methylsulfate, ethylsulfate, p-toluenesulfonate, etc.); and Z and Z_1 each represents the nonmetallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of a thiazole nucleus (e.g., thiazole, methylthiazole, phenylthiazole, etc.), a benzothiazole nucleus (e.g., benzothiazole, 6-chlorobenzothiazole, 6-methylbenzothiazole, etc.), a naphthothiazole nucleus e.g., α or β-naphthothiazole, 5-ethoxy-βnaphthothiazole, etc.), an oxazole nucleus (e.g., 4-methyloxazole, 4-phenyloxazole, etc.), a benzoxazole nucleus (e.g., benzoxazole, 6-chlorobenzoxazole, etc.), a naphthoxazole nucleus e.g., α or β-naphthoxazole, 5-methoxy-β-naphthoxazole, etc.), a selenazole nucleus (e.g., selanazole, 4-methyselenazole, 4-phenylselenazole, etc.), a benzoselanazole nucleus (e.g., benzoselenazole, 5-chlorobenzoselenazole, etc.), a naphthoselenazole nucleus (e.g., α or β-naphthoselenazole, 5-ethoxy-β-naphthoselenazole, etc.), a 2-quinoline nucleus (e.g., quinoline, 5-methylquinoline, 6-chloroquinoline, etc.), a 4-quinoline nucleus (e.g., quinoline, 6-methoxyquinoline, etc.), a 1-isoquinoline nucleus (e.g., isoquinoline, 3,4-dihydroisoquinoline, etc.), and a 3,3-dialkylindolenine nucleus (e.g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, etc.), provided that at least one of the groups R, R_1, R_2, Z, or Z_1 contains a sulfo group (e.g., sulfo, sulfoalkyl such as ω-sulfoethyl, ω-sulfopropyl, etc.) or a carboxy group (e.g., carboxy, ω-carboxyethyl, ω-carboxypropyl, etc.).

Those skilled in the art of dye sensitization will readily appreciate that the anhydronium bases of the above dyes will be equally effective as near infrared-sensitizing dyes for zinc oxide. The anhydronium bases are regarded as being derived from the above general formula by the loss of a mole of HX or MX wherein X has been defined above and M is a metallic atom such as sodium, potassium, etc. The anhydronium bases of the above dyes are within the scope of the present invention.

BRIEF DESCRIPTION OF THE DRAWING

FIGS. 1 and 2 represent the curves obtained when electrophotographic layers containing infrared-sensitizing dyes were tested for electrophotographic speed in a dynamic capacitance electrometer.

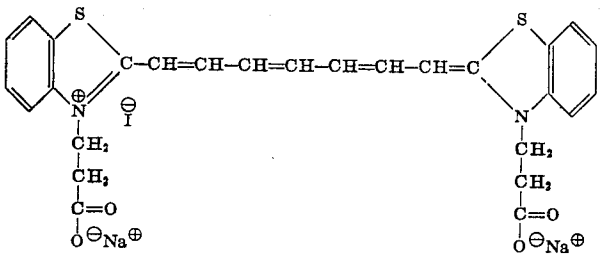
FIG. 3 represents the curve obtained when an electrophotographic layer containing a conventional sensitizing dye was

tested for electrophotographic speed in a dynamic capacitance electrometer.

DETAILED DESCRIPTION

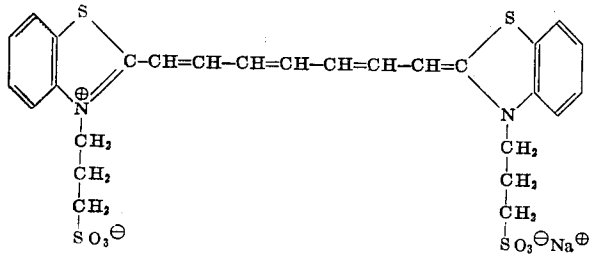
The invention will be described in greater detail with the aid of the following examples. Three heptamethine cyanine dyes, and their preparations, will be disclosed as illustrative of the kinds of dyes that may be used to practice the present invention.

SYNTHESIS OF [2-BIS (3- ω-CARBOXYETHYL BENZOTHIAZOLYL)] HEPTAMETHINE CYANINE IODIDE (IR-1)



To 600 ml. of absolute ethanol were added 70 g. of 2-methyl-3-(ω-carboxyethyl) benzothiazole iodide (0.2 mole) and 30 g. of glutaconic dianil hydrochloride (0.11 mole), and the mixture thereof was heated to its boiling point, about 85° C. The heating was then discontinued and 30 g. of sodium ethylate in 150 ml. of absolute alcohol were slowly added over a period of time of about 5 minutes. The reaction was allowed to continue for an additional 10 minutes, and the product was allowed to cool to and was kept at room temperature for about 36 hours. The product was then placed in a refrigerator set at about -10° C. for about 24 hours, and blue-black dye precipitated. The dye was filtered, suspended in ether three times, then in ethanol, and finally in ether. The yield of dye was about 100 g. The dye melted over a temperature range of about 218° to 230° C. The principal absorption maximum, as measured on a DK-2A Absorption Spectrophotometer, for the dye appeared at 760 millimicrons in dilute dimethyl sulfoxide. When absorbed on zinc oxide, the absorption maximum, as measured on a DK-2A Reflectance Spectrophotometer, was about 780 millimicrons. An analysis of the infrared spectrum of the dye, obtained with a Perkin-Elmer 521 Grating Infrared Spectrophotometer, indicated Hthat most of the dye was present as the sodium salt of the carboxylic acid. However, the dye has also been prepared in the form of the free carboxylic acid in which form it is equally as effective as an infrared-sensitizer for zinc oxide.

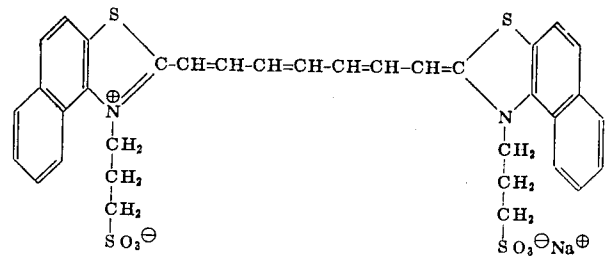
SYNTHESIS OF [2-BIS (3 ω-SULFOPROPYL BENZOTHIAZOLYL] HEPTAMETHINE CYANINE (IR-2)



To 50 ml. of dry ethanol were added 5.42 g. of 2-methyl-3-(ω-sulfopropyl) benzothiazole (0.02 mole) and 2.84 g. of glutaconic dianil hydrochloride (0.01 mole), and the mixture was brought to a boil. The heating was then discontinued and 1.5 g. of sodium ethylate in 30 ml. of dry ethanol were slowly added over a period of time of about 5 minutes. The mixture was heated at about 85° C. for about 5 minutes, then allowed to cool to and remain at room temperature in the dark for about 60 hours. The mixture was then refrigerated at about -10° C. for about 24 hours. The crude dye which precipitated was filtered, washed with 200 ml. of ethanol, and dried with ether. The yield was about 7.5 g. The dye melted at about 198°–200° C. The principal absorption maximum for the dye appeared at 770 millimicrons in dilute ethanol. When absorbed on zinc oxide, the absorption maximum was about 800 millimicrons. An analysis of the infrared spectrum of the dye indicated that the cyanine dye was obtained in the form of sodium salt of the sulfonic acid. However, the dye has also been prepared in the form of the free sulfonic acid and has been found to be equally as effective as an infrared-sensitizing dye for zinc oxide.

Dyes IR-1 and IR-2 are the preferred dyes for the purposes of the present invention. However, as will be readily appreciated in view of this disclosure, other polymethine dyes having the general structure described previously can be used to sensitize zinc oxide in the near infrared region of the spectrum.

SYNTHESIS OF [2-BIS (3 ω-sulfopropyl β-NAPHTHOTHIAZOLYL)] HEPTAMETHINE CYANINE (IR-3)



To 30 ml. of dry ethanol were added 3.25 g. of 2-methyl-3-(ω-sulfopropyl) β-naphthothiazole (0.01 mole) and 1.45 g. of glutaconic dianil hydrochloride (0.005 mole), and the mixture was heated to approximately 85° C. The heating was then discontinued and 0.5 g. of sodium ethylate in 10 ml. of dry ethanol were slowly added, with stirring, over a period of time of about 5 minutes. The reaction mixture turned red, then slowly turned to dark green. It was kept in the dark at room temperature for about 16 hours and then refrigerated at about -10° C. for about 20 hours. The crude dye which precipitated was filtered, washed with 200 ml. of cold ethanol, then was suspended in warm ethanol, filtered, and rinsed first with cold ethanol and finally with ether The yield was about 3.1 g. The dye melted over a temperature range of about 218° to 235° C. The principal absorption maximum for the dye appeared at 803 millimicrons in methanol. When adsorbed on zinc oxide, the absorption maximum appeared at about 700 millimicrons, and the band extended to about 900 millimicrons.

The infrared-sensitizing dyes of the present invention can be combined with zinc oxide photoconductive material in any of the conventional manners to produce photoconductive coatings. No special binders are needed and any of the high dielectric-insulator binders known for photoconductive coatings may be used, such as styrene-butadiene copolymers, silicone resins, styrene-alkyd resins, silicone-alkyd resins, soya-alkyd resins, polyvinyl chloride, polyvinyl acetate, paraf-

fin and mineral waxes. Nonpolar solvents, such as aromatic hydrocarbons, are preferred in preparing the photoconductive layers. The photoconductive coatings can be applied to any suitable substrate in conventional manner and then dried to produce the desired photoconductive layers. The following examples will aid in the description of the present invention.

EXAMPLES 1–3

Electrophotographic coatings were prepared and the near infrared-sensitizing dyes IR–1 and IR–2 were used to sensitize zinc oxide. One hundred parts by weight zinc oxide (Photox 80) were mixed with 15 parts resin (DeSoto 7209, a styrenated-alkyd resin), and reagent grade toluene was added to adjust the mixture to about 60 percent total solids. The mixture was intimately mixed in a Waring Blender for 5 minutes. To this mixture was added a solution of either dye IR–1 or IR–2 in methanol. In the case of dye IR–1 used in example 1, the amount of dye added was 4×10^{13} g. of dye per 100 g. of zinc oxide, and in the case of dye IR–2 used in example 2, the amount of dye added was 6×10^{13} g. of dye per 100 g. of zinc oxide. The mixtures of coatings were then stirred with a magnetic stirrer for about 2 minutes to allow in each case the dye to adsorb onto the zinc oxide.

The coatings were applied to aluminum foil with a Baker film applicator. The coat weight was maintained at about 20 pounds per ream (500 sheets, 25 by 38 inches). After drying, the coated products were conditioned in the dark for 24 hours at 50percent relative humidity at 74° F.

After conditioning, the products were tested for electrophotographic speed in a dynamic capacitance electrometer containing a Kodak filter No. 7–69 and utilizing 30 foot candles of tungsten illumination. By using this filter, only light above 710 millimicrons was transmitted with approximately 75 percent of the light transmitted at 820 millimicrons. A dynamic capacitance electrometer measures the electrophotographic properties of a zinc oxide coating, for example, charge acceptance, dark decay, light decay, and residual charge after exposure. These measurements are recorded on an oscilloscope and photographed to obtain a trace of the electrophotographic properties. FIGS. 1 and 2 represent the traces obtained for the electrophotographic layers of examples 1 and 2 and from the traces it is evident that these coatings were photosensitive in the near infrared region of the spectrum.

A third product was prepared as above, except that the sensitizing dye used was an excellent conventional sensitizing dye, bromophenol blue. The dye was used in example 3 in the amount of 4×10^{13} g. of dye per 100 g. of zinc oxide. Under the conditions set out above, the photoconductive layer did not discharge in the electrometer. This was to be expected since bromophenol blue absorbs light at 610 millimicrons in a zinc oxide coating, and with the Kodak 7–69 filter, no light was transmitted to the zinc oxide layer at this wavelength. FIG. 3 represents the electrometer curve obtained when bromophenol blue was used as the sensitizing dye for zinc oxide.

Similar experiments were performed using an SCM Model 33 copier, modified by placing a Kodak 7–69 filter in front of the lens, and between the light source and the electrophotographic layer. The electrophotographic coatings of examples 1, 2 and 3 were applied to paper at a coat weight of about 20 pounds per ream. The dried products were exposed in the copier, and those papers coated with the coatings of examples 1 and 2 printed to give electrophotographic reproductions of an original. However, the paper having the coating of example 3, wherein the photoconductive layer was sensitized to visible light with bromophenol blue, failed to print regardless of the dye level used.

We have also found that the intensity of the exposing source can be reduced if zinc oxide is sensitized in the near infrared region. An SCM Model 33 copier was connected so that the exposure lamps were in series and operated from a Variac to vary the voltage to the lamps. A constant shutter setting (designated 5) was used, and paper samples bearing the coatings of examples 1 and 3 were exposed at varying Variac settings. At a dye level of 6×10^{13} g. of dye per 100 g. of zinc oxide, the photoconductive layer containing IR–1 produced a print when the voltage to the exposing source was reduced to half the normal amount, whereas the photoconductive layer containing bromophenol blue, at the same dye concentration, would not print. By reducing the voltage to the exposure source to one-half, the power input was reduced to one-fourth and, consequently, the light output was reduced to about one-fourth.

Paper coated with the coatings of examples 1–3 were tested for luminosity as measured on a Martin-Sweets Color Brightness Instrument. Luminosity is a measure of the average visible reflectance of the paper over the visible region of the spectrum. At the same electrophotographic speed, the coatings containing dyes IR–1 and IR–2 had at least five points higher luminosity than the coating prepared with bromophenol blue.

EXAMPLE 4

An electrophotographic coating was prepared in similar manner to that described above in connection with examples 1–3. In this instance, the near infrared-sensitizing dye IR–3 was used in an amount of about 2×10^{12} g. of dye per 100 g. of zinc oxide. The coating was applied to paper with a Baker film applicator at a coat weight of about 20 pounds per ream.

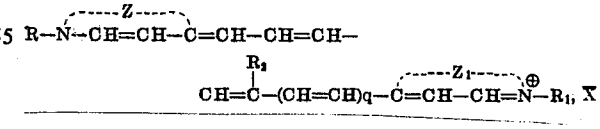
The dried, coated paper was exposed in an SCM Model 33 copier equipped with a Kodak 7–69 filter in front of the lens. A print of an original was produced on the electrophotographic layer, evidencing that the zinc oxide has been sensitized in the near infrared region of the spectrum by dye IR–3.

From the above examples, it can be seen that photoconductive zinc oxide can be sensitized for response in the infrared region of the spectrum. Such photoconductive compositions as described comprise photoconductive zinc oxide, a high dielectric insulator binder for the zinc oxide, and adsorbed to the surface of the zinc oxide a near infrared-sensitizing dye.

As one skilled in the art will readily appreciate, various modifications may be made in the examples and descriptions set out above without departing from the spirit of the invention or the scope of the appended claims.

We claim:

1. A photoconductive composition comprising photoconductive zinc oxide, a high dielectric insulator binder for the zinc oxide, and adsorbed to the surface of the zinc oxide a cyanine dye for sensitizing the zinc oxide in the near infrared region of the spectrum, said cyanine dye selected from those represented by the following general formula:



wherein R and R_1 each represents a member selected from a sulfoalkyl group or a carboxyalkyl group; R_2 represents a member consisting of a hydrogen atom; q represents a unit positive integer; X represents an acid anion; and Z and Z_1 each represents the nonmetallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of a benzothiazole nucleus, or a naphthothiazole nucleus.

2. A photoconductive composition as defined in claim 5 in which the near infrared-sensitizing cyanine dye is an anhydronium base of the dyes defined in claim 1.

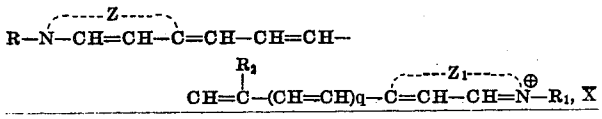
3. A photoconductive composition as defined in claim 1 in which the near infrared-sensitizing cyanine dye is [2-bis (3 ω-carboxyethyl bezothiazolyl] heptamethine cyanine iodide.

4. A photoconductive composition as defined in claim 1 in which the near infrared sensitizing cyanine dye is [2-bis(3- ω-sulfopropyl benzothiazolyl)] heptamethine cyanine.

5. A photoconductive composition as defined in claim 1 in which the near infrared-sensitizing cyanine dye is [2-bis (3-ω-sulfopropyl β-naphthothiazolyl)] heptamethine cyanine.

6. A photoconductive composition as defined in claim 1 in which the near infrared-sensitizing cyanine dye renders the zinc oxide photosensitive to wavelengths of light above 700 millimicrons.

7. The process of producing a photoconductive composition which photosensitive in the near infrared region of the spectrum which comprises the step of mixing photoconductive zinc oxide with a high dielectric insulator binder, and add to the mixture a near infrared-sensitizing cyanine dye selected from those dyes represented by the following general formula:



wherein R and R_1 each represents a member selected from a sulfoalkyl group or a carboxyalkyl group; R_2 represents a

member consisting of a hydrogen atom; q represents a unit positive integer; X represents an acid anion; and Z and Z_1 each represents the nonmetallic atoms necessary to complete a heterocyclic nucleus selected from a benzothiazole nucleus, or a naphthothiazole nucleus, whereby the dye is adsorbed onto the surface of the zinc oxide and renders the zinc oxide photosensitive to wavelengths of light above 700 millimicrons.

8. The process of claim 7 in which the near infrared-sensitizing cyanine dye is an anhydronium base of dyes defined in claim 7.

9. The process of claim 7 in which the near infrared-sensitizing cyanine dye is [2-bis (3- ω-carboxyethyl benzothiazolyl)] heptamethine cyanine iodide.

10. The process of claim 7 in which the near infrared-sensitizing cyanine dye is [2-bis (3- ω-sulfopropyl benzothiazolyl)] heptamethine cyanine.

11. The process of claim 7 in which the near infrared-sensitizing cyanine dye is [2-bis (3- ω-sulfopropyl β-naphthothiazolyl)] heptamethine cyanine.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,619,154 Dated November 9, 1971

Inventor(s) Giancarlo A. Cavagna et al

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 7, "absorbed" should read -- adsorbed --.

Column 2, lines 12-17, the minus charge designation over the anion element of the general formula is not clear and should read as follows: $\ominus$ -- X --; line 38, "5-ethoxy-β naphthothiazole" should read -- 5-ethoxy-β-naphthothiazole --.

Column 3, example 1 of the dye, the title of the structure (IR-1) should read: -- [2-BIS (3-{ω-CARBOXYETHYL} BENZOTHIAZOLYL)] --. Column 3, line 41, -- a -- should be inserted before "blue-black"; line 48, "absorbed" should read -- adsorbed --; line 52, "Hthat" should read -- that --; example 2 of the dye, the title of the structure (IR-2) should read:
-- [2-BIS (3-{ω-SULFOPROPYL} BENZOTHIAZOLYL)] --.

Column 4, line 14, "absorbed" should read -- adsorbed --; line 18, -- the -- should be inserted before "sodium"; example 3 of the dye, the title of the structure (IR-3) should read:
-- [2-BIS (3-{ω-SULFOPROPYL}β-NAPHTHOTHIAZOLYL)] --.

Column 5, line 15, "Blender" should read -- Blendor --; line 19, "4 X 10^{13}" should read -- 4 X 10^{-3} --; line 20, "6 X 10^{13}" should read -- 6 X 10^{-3} --; line 43, a comma -- , -- should be inserted after "2"; line 50, "4 X 10^{13}" should read -- 4 X 10^{-3} --.

Column 6, line 4, "6 X 10^{13}" should read -- 6 X 10^{-2} --; line 27, "2 X 10^{12}" should read -- 2 X 10^{-2} --; claim 1, the minus charge designation over the anion element of the general formula is not clear and should read as follows: $\ominus$ -- X --; line 63, "nonmetallic" should read -- non-metallic --; line 67, "5" should read -- 1 --; lines 71-72, "[2-bis (3ω-carboxyethyl bezothiazolyl]" should read -- [2-bis (3-{ω-carboxyethyl} benzothiazolyl)] --; lines 74-75, "[2-bis (3-ω-sulfopropyl benzothiazolyl)]" should read -- [2-bis (3-{ω-sulfopropyl} benzothiazolyl)] --.

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

Column 7, lines 2-3, "[2-bis (3- ω -sulfopropyl β -naphthothiazolyl)]" should read, -- [2-bis (3- {ω -sulfopropyl} β -naphthothiazolyl)] --; line 9, -- is -- should be inserted before "photosensitive"; line 10, "step" should read -- steps --; line 11, "add" should read -- adding --; claim 7, the minus charge designation over the anion element of the general formula is not clear and should read as follows: $\overset{\ominus}{X}$ --.

Column 8, line 3, "nonmetallic" should read -- non-metallic --; line 12, "[2-bis (3- ω -carboxyethyl benzothiazolyl)]" should read -- [2-bis (3- {ω -carboxyethyl} benzothiazolyl)] --; lines 15, 16 "[2-bis (3- ω -sulfopropyl benzothiazolyl)]" should read -- [2-bis (3- {ω -sulfopropyl} benzothiazolyl)] --; lines 18, 19 "[2-bis (3- ω -sulfopropyl β -naphthothiazolyl)]" should read -- [2-bis (3- {ω -sulfopropyl} β -naphthothiazolyl)] --.

Signed and sealed this 15th day of February 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents