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METHOD FOR INCREASING PHOTOSENSITIVITY OF PHOTOCONDUCTIVE MATERIALS

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FIG. 1

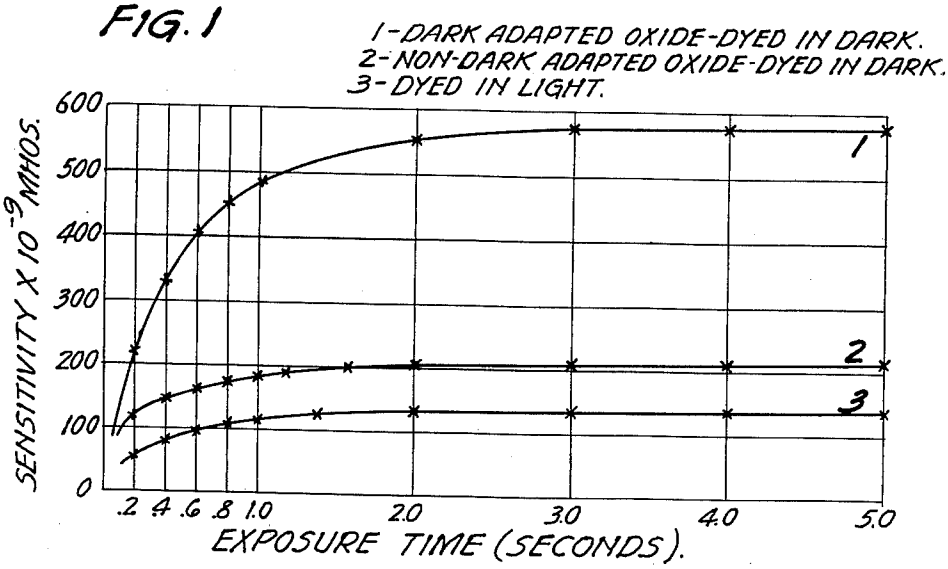
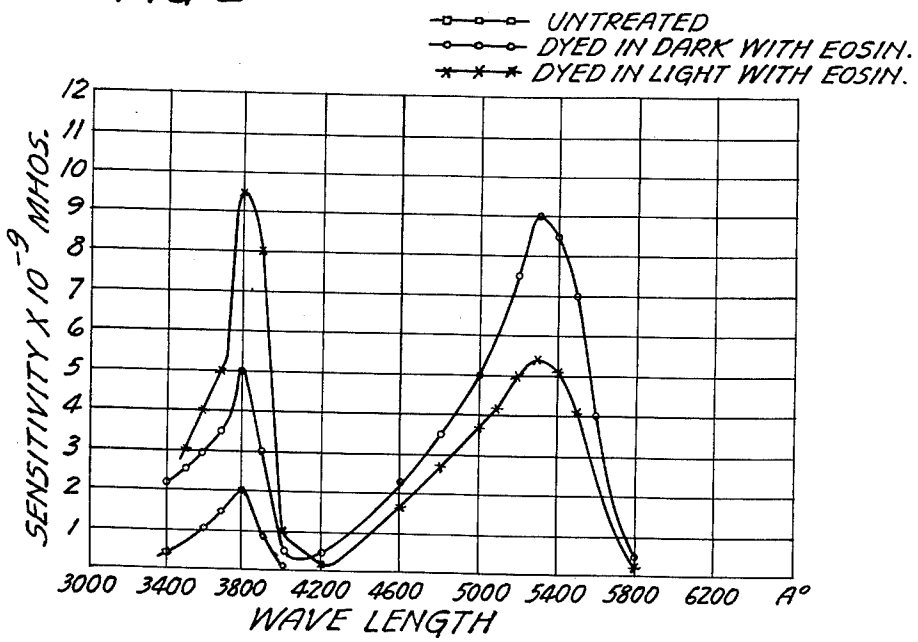


FIG. 2



INVENTOR
BENJAMIN L. SHELY

BY
Carpenter, Abbott, Coulter & Kinney
ATTORNEYS

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METHOD FOR INCREASING PHOTOSENSITIVITY OF PHOTOCONDUCTIVE MATERIALS

Benjamin L. Shely, Mahtomedi, Minn., assignor to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware

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This invention relates to a method for increasing the light sensitivity and response rate of photosensitive materials. In one aspect it relates to an improved process for the dye sensitization of photoconductive materials. In another aspect it relates to a process for increasing the spectral response characteristics of a photoconductive material.

The use of photosensitive sheet materials having surface layers which become electrically conductive when irradiated with light of certain wave lengths is known. Thus, a photoconductive material such as zinc oxide can be coated on a sheet of an electrically conductive material, exposed to a light image, and subjected to electrolysis in the presence of various developer solutions, such as an aqueous silver nitrate solution. The differential conductivity pattern produced by illumination with the light image is thereby electrolytically developed to form a visible reproduction of the original image.

Although the above process is capable of producing permanent visible reproductions having good detail and contrast, it has been found that the photoconductive materials are sensitive to light only within relatively narrow ranges of wavelength. It has also been found that increased "breadth" of spectral sensitivity is afforded by the physical incorporation of certain optical sensitizers or dyes into the photoconductive material, customarily by addition of the dyes to a dispersion of zinc oxide in a resin solution before depositing on an electrically conductive backing or by ball milling with the zinc oxide-resin mix. However, the spectral sensitivity still requires the use of relatively high light intensities and/or long exposures to reproduce a visible image.

It is therefore an object of this invention to improve the sensitivity and response rate of a photoconductive material.

Another object of this invention is to provide a process for increasing the optical sensitivity of a photoconductive material.

Still another object of this invention is to improve the sensitivity of a photoconductive copy sheet.

Yet another object of this invention is to provide a simple, efficient and economical method for improving the spectral response of a photoconductive material.

In accordance with this invention, the optical or light sensitivity and photoresponse characteristics of a photoconductive material, such as zinc oxide and indium oxide, are improved by dark adapting the material and subsequently treating the photoconductive particulate material in the dark with a mixture of an optical sensitizer and a partial solvent for said optical sensitizer. By "partial solvent" is meant an organic liquid in which the optical sensitizer employed is only slightly soluble, most preferably of the order of magnitude of 10^{-2} to 10^{-6} moles of dye per liter at 20° C., said organic liquid having a dielectric constant as hereinafter defined.

As mentioned earlier, the use of optical sensitizers, i.e. organic compounds which give up electrons when excited by light of certain wavelengths, is known. The difficulty in their utilization has been to obtain adequate concentrations of the sensitizer at the surface of the photoconductive material. It has now been found that a period of dark adaptation, i.e. 24 hours or more, of the photoconductive material coupled with the step of incorporating the optical sensitizer into the photoconductive material in a dark environment greatly increases the optical sensitivity and photoresponse of the photoconductor, often by a factor of 2 or more.

The optical sensitivity and photoresponse characteristics of the photoconductive material are also enhanced by carrying out the step of incorporating the optical sensitizer into the photoconductive material in the presence of a partial solvent for the optical sensitizer. Although the mechanism is not fully known, it is believed that the partial solvent may function as a carrier, permitting the solubilization of relatively small quantities of the sensitizer, in which solubilized form absorption on the active surface sites of the photoconductive particles is greatly facilitated. However, when the carrier or sensitizing medium is too good a solvent for the optical sensitizer it apparently tends to compete with the photoconductive material for the sensitizer and thus to limit the amount of sensitizer absorbed or taken up by the photoconductive surface, or perhaps to compete with the sensitizer for dyeable sites on the photoconductive particles. Irrespective of the mechanism involved, the techniques of this invention produce a surprising increase in the sensitivity and rate of response of the dyed photoconductors.

Various optical sensitizers for photoconductive powders are known. Generally, oil insoluble organic dyes are most effective, particularly those dyes selected from the following classes:

Acridine dyes, e.g.: Phosphine R (46045)
Xanthene dyes, e.g.:
- Eosin Y (45380)
- Erythiosin (45430)
- Rose Bengal (45435)

Diphenylmethane dyes, e.g.: Auramine (41000)
Triphenylmethane dyes, e.g.:
- Calcozine Violet C (42555)
- Erio Chrome Cyanine R (42571)

Stilbene dyes, e.g.:
- Stilbene Yellow G (40000)
- Diphenyl Fast Orange 4RL (40265)

Thiazoles, e.g.:
- Seto-flavine T (49005)
- Primuline NAC (49000)

Quinoline dyes, e.g.:
- Calcocid Yellow CW (47005)
- Calcomine Chinoline Yellow P (47035)

Sulfur dyes, e.g.:
- Sulfogene Bordeaux 5CF (53720)
- Calcogene Yellow 2GCF (53160)

Azo dyes, e.g.:
- Azo Scarlet Y (17755)
- Diazophenyl Fast Scarlet G1 (17805)

The dye identification numbers above are taken from the second volume of Color Index (1956). Other sensitizing dyes are described in Canadian Patents Nos. 576,733 and 576,734.

The partial solvent is selected with particular regard for the specific optical sensitizer to be used. However, generally those organic solvents having a dieelectric constant between 5 and 20, preferably between 5 and 18, are useful as partial solvents for the oil insoluble dye sensitizers. The preferred partial solvents include butyl alcohol, methyl acetate, ethyl acetate, butyl acetate, propyl acetate, methyl ethyl ketone, etc., with esters, especially acetates, having from 3 to 6 carbon atoms, being particularly preferred. Solvents such as toluene, benzene, heptane, ethyl ether, carbon tetrachloride, methyl alcohol, have been found to be unsatisfactory as partial solvents. Reagent grade materials are desirable, though not essential, since the presence of impurities can adversely effect the characteristics of the photoconductive powder.

After the photoconductive powder has been dark adapted it is suspended in the partial solvent, and the optical sensitizer—usually dissolved in a small quantity of a good solvent therefor which has a dielectric constant above about 25 (e.g. methyl alcohol), which is miscible with the partial solvent and which has better solvent properties for the optical sensitizer than the particular partial solvent with which it is to be employed—is added to the suspension. Following a thorough mixing under continued dark conditions the powder is filtered and dried.

The following example is illustrative of the above techniques. 0.5 gram of Eosin Y, a xanthene dye, was completely dissolved in 99.5 grams of ethyl alcohol. Two grams of zinc oxide powder were added to 50 ml. of ethyl acetate containing 5 drops (.25 ml.) of the above Eosin Y solution and the admixture was shaken thoroughly. The zinc oxide was filtered out and dried, and a pressed powder sample was prepared for measurement of the photoresponse characteristics. The pressed powder test was conducted as follows.

Two aluminum electrodes, 3 cm. wide and 0.063 cm. thick, are mounted on a Lucite block. The electrodes are parallel spaced in such a fashion as to create a sample holder therebetween, which sample holder cavity has a flat bed and perpendicular aluminum walls and is 3 cm. long and 0.63 cm. wide. Two hundred milligrams of the photoconductive powder to be tested are placed uniformly in the cavity and compressed with a plunger of substantially the same cross-sectional area as the cavity, using a pressure of about 204 pounds per square inch. This forms a compacted layer of photoconductive powder about 0.05 cm. thick which is pressed firmly against the aluminum electrode walls. During testing the sample holder is enclosed in a dry box containing a dessicant. A D.C. test voltage is applied across the sample and across a series resistance, with provision made for current measurement. The series resistance is adjusted and kept at a small value as compared to the sample resistance, thus impressing all but a negligible portion of the test voltage across the sample. The small voltage drop across the series resistance is amplified and recorded, and the conductance or conductivity then calculated. The conductivities thus calculated on the basis of the current measurement and the sample geometry are the effective conductivities which would exist if the conductivity were uniform throughout. The dark conductivities are calculated from the current measurements on the unilluminated sample, and the photoconductivity values are calculated from the current measurements after 5 seconds of illumination from a 200 watt tungsten light source operating at a color temperature of 3100° K. and placed at such a distance that about .0045 watt per square centimeter of radiant energy falls on the sample. About 0.001 watt per square centimeter of this energy is in the visible region between 0.38 and 0.70 micron wavelength.

Using the above techniques, three samples of zinc oxide powder were dye sensitized. Sample 1 was dark adapted and was dye sensitized under dark conditions. Sample 2 was dye sensitized under dark conditions without a prior period of dark adaptation. Sample 3 was dye sensitized under light conditions without a prior period of dark adaptation. FIGURE 1 shows the effect of these techniques on a plot of light conductance versus exposure time, using the earlier mentioned light source. It was noted that dye sensitization under dark conditions, particularly of the dark adapted photoconductive material, produced a material with higher light conductance and with a faster rate of response. Similar results are obtained with photoconductive indium oxide powders.

The photoconductive materials produced in accordance with this invention not only have a higher light conductance value and a more rapid response rate but also possess superior spectral sensitivity, i.e. are sensitive to light from a greater portion of the spectrum. This is illustrated by FIGURE 2, wherein sample 1 represents an untreated sample of zinc oxide, sample 2 represents a zinc oxide sample dyed with Eosin Y (as set forth earlier) under light conditions, and sample 3 represents a zinc oxide sample similarly dyed with Eosin Y under dark conditions. The data was obtained by placing a standard pressed powder sample 3 inches from a Bausch and Lomb grating monochromator (Model PD–21) in which the lamp was set at high intensity with the slit completely open. The conductance of the powder was measured over a range from 3000–7000 A., and the sample was allowed to reach a saturation value at each measured wavelength, i.e. every 100 A. Although the intensity was not the same at the various wavelengths, the relative effect of dye sensitization under light and dark conditions was observed.

With the 5 second exposure technique described earlier various solvents were evaluated as "partial solvents," the results of which appear in Table I.

Table I

Partial solvent	Light conductance (sensitivity), mhos	Partial solvent dielectric constant
ethyl acetate	580×10^{-9}	6.02
methyl acetate	520×10^{-9}	8.0
butyl acetate	420×10^{-9}	5.0
propyl acetate	490×10^{-9}	8.1
methyl ethyl ketone	460×10^{-9}	18.8
butyl alcohol	410×10^{-9}	17.00
ethyl alcohol	240×10^{-9}	24.3
acetone	250×10^{-9}	20.70
chloroform	120×10^{-9}	4.80
carbon tetrachloride	55×10^{-9}	2.24
methyl alcohol	70×10^{-9}	32.6
heptane	70×10^{-9}	1.92
ethyl ether	44×10^{-9}	4.34
benzene	11×10^{-9}	2.28
toluene	16×10^{-9}	2.38
water	6.5×10^{-6}	78.00
no dye treatment	7×10^{-9}	

It is apparent from the data obtained that a period of dark adaptation of the photoconductive material prior to dye sensitization produces a significant improvement in the light sensitivity or light conductance values. It is also apparent that dye sensitization under dark conditions enhances the light sensitivity. Furthermore, the sensitivity and photoresponse characteristics, particularly the rate of response, are significantly increased when the optical sensitizer or dye is incorporated into the photoconductive powder in the presence of a partial solvent having a dielectric constant between 5 and 20, as herein defined.

Variations and modifications will become apparent to persons skilled in the art from this disclosure, and the illustrative examples are intended only to exemplify the best embodiment of this invention and not to limit the scope thereof.

I claim:

1. A method for increasing the light sensitivity and photoresponse characteristics of a photoconductive powder selected from the group consisting of zinc oxide and indium oxide which comprises dark adapting said photoconductive powder for at least 24 hours, contacting said photoconductive powder in the absence of light with an optical sensitizer therefor selected from the oil insoluble organic dye group consisting of acridine dyes, xanthene dyes, diphenylmethane dyes, triphenyl methane dyes, stilbene dyes, thiazole dyes, quinoline dyes, sulfur dyes and azo dyes, in a partial solvent media, said partial solvent being a liquid organic compound capable of dissolving only between about 10^{-2} and 10^{-6} moles of said optical sensitizer per liter at 20° C. and having a dielectric constant between 5 and 18, and subsequently drying said photoconductive powder.

2. The method of claim 1 wherein said photoconductive material is zinc oxide powder.

3. The method of claim 1 wherein said photoconductive material is indium oxide powder.

4. A method for increasing the light sensitivity and photoresponse characteristics of zinc oxide powder which comprises contacting said zinc oxide under dark conditions with an organic oil insoluble optical dye sensitizer therefor in a partial solvent media, said partial solvent being a liquid organic compound with a dielectric constant between about 5 and about 20 and being capable of dissolving only between about 10^{-2} and 10^{-6} moles of said optical sensitizer per liter at 20° C.

5. A method for increasing the light sensitivity and photoresponse characteristics of photoconductive indium oxide powder which comprises contacting said photoconductive indium oxide under dark conditions with an organic oil insoluble optical dye sensitizer therefor in a partial solvent media, said partial solvent being a liquid organic compound with a dielectric constant between about 5 and about 20 and being capable of dissolving only between about 10^{-2} and 10^{-6} moles of said optical sensitizer per liter at 20° C.

6. A method for increasing the light sensitivity and photoresponse characteristics of a photoconductive material selected from the group consisting of zinc oxide and indium oxide which comprises contacting said photoconductive material in the absence of light with an organic oil insoluble optical dye sensitizer therefor in a partial solvent media, said partial solvent being a liquid organic compound with a dielectric constant between about 5 and about 20.

7. A method for increasing the light sensitivity and photoresponse characteristics of a photoconductive material selected from the group consisting of zinc oxide and indium oxide which comprises dark adapting said photoconductive material for at least 24 hours and thereafter contacting said photoconductive material in the absence of light with an organic oil insoluble optical dye sensitizer therefor in a partial solvent media, said partial solvent being a liquid organic compound with a dielectric constant between about 5 and about 20 and being capable of dissolving only between about 10^{-2} and 10^{-6} moles of said optical sensitizer per liter at 20° C.

8. A method for increasing the light sensitivity and photoresponse characteristics of a photoconductive powder selected from the group consisting of zinc oxide and indium oxide which comprises dark adapting said photoconductive powder for at least 24 hours, contacting said photoconductive powder in the absence of light with an organic, oil insoluble optical dye sensitizer therefor in a partial solvent media, said partial solvent being a liquid organic compound capable of dissolving only between about 10^{-2} and 10^{-6} moles of said optical sensitizer per liter at 20° C. and having a dielectric constant between about 5 and about 20, and subsequently drying said photoconductive powder.

9. The process of claim 8 in which the partial solvent is an ester having from 3 to 6 carbon atoms.

10. The process of claim 8 in which the partial solvent is ethyl acetate.

11. The process of claim 8 in which the partial solvent is methyl acetate.

12. The process of claim 8 in which the partial solvent is butyl acetate.

13. The process of claim 8 in which the partial solvent is butyl alcohol.

14. The process of claim 8 in which the partial solvent is methyl ethyl ketone.

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