United States Patent

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[54] BIANTHRONE COMPOUNDS AS SENSITIZERS FOR ORGANIC PHOTOCONDUCTIVE SYSTEMS

7 Claims, No Drawings

[52] **U.S. Cl.** **96/1.5,**
96/1, 252/501, 260/351

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G03g 5/06

[50] **Field of Search** 96/1.5, 1.6,
1; 252/501

[56] **References Cited**

UNITED STATES PATENTS

3,252,794	5/1966	Schaum et al.	96/1
3,287,119	11/1966	Hoegl	96/1.5
3,408,190	10/1968	Mammino	96/1.5
3,441,410	4/1969	Brynko	96/1.1
3,451,811	6/1969	Brynko	96/1

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ABSTRACT: Bianthrone compounds including those having halogen, lower alkyl and hydrogen substituents in the ring structure, are used to sensitize organic photoconductive systems so that they will respond to electromagnetic radiation in the visible portion of the spectrum. Typical of the sensitizers that can be used are 2,2'-dibromobianthrone and bianthrone.

BIANTHRONE COMPOUNDS AS SENSITIZERS FOR ORGANIC PHOTOCONDUCTIVE SYSTEMS

BACKGROUND OF THE INVENTION

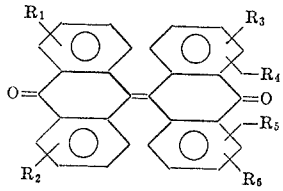
This invention relates generally to sensitizers for organic photoconductive members, and in particular, relates to the addition of bianthrone-type compounds for the purpose of increasing the sensitivity range to electromagnetic radiation in the visible portion of the spectrum.

In the photoelectrostatic copying art, a recording member is prepared by applying a photoconductive layer to a conductive support. A large number of organic compounds are known to have utility in electrophotographic systems such as aromatic compounds which may include naphthalene, biphenyl, fluorene, anthracene, phenanthrene, acenaphthene, chrysene, diphenylamine, and carbazole; polymeric organic photoconductors which include polystyrenes, polyvinylxylenes, polyvinylcarbazoles, poly-α-vinylnaphthalene, polyindene and polycarbonates. In this art it is conventional to use polymeric-type organic photoconductors as well as monomeric materials with the former polymerizing to form a continuous film and the latter being dispersed in film forming binders. In their unsensitized condition, the organic photoconductive materials in most instances are known to have a rather slow response to electromagnetic radiation in the visible range, being more sensitive to radiation in the ultraviolet region of the spectrum.

The construction of photoelectrostatic reproduction equipment to process the organic photoconductive-type members is greatly simplified if conventional filament-type sources of illumination can be used rather than the mercury vapor-type lamps which are the standard source of ultraviolet radiation. The broadening of the spectral response range of these organic photoconductors to include the visible range of the spectrum may be accomplished by the addition of certain additives.

SUMMARY OF THE INVENTION

It has been found that members from the class of compounds having the following general formula:



wherein R_1, R_2, R_3, R_4, R_5, and R_6 represent lower alkyl, halogen, and hydrogen substituents, and R_1, R_2, R_3, R_4, R_5, and R_6 can be the same or different, extend the photo response of organic photoconductive systems into the visible portion of the spectrum.

It is the general object of this invention to provide an improved organic photoconductive member which is sensitized to respond to the visible region of the spectrum through the use of a dimerized anthrone derivative.

DESCRIPTION OF PREFERRED EMBODIMENT

In carrying out the object of the invention, the sensitizer is added to the solution containing the polymeric photoconductive material or to the dispersion in which the crystals of photoconductive material are dispersed in a resin binder. To the combination of the organic photoconductor solution or dispersion there is added in the range of 0.2 percent to 100 percent by weight of sensitizer based on the weight of the organic photoconductive material in order to extend the photoresponse of the photoconductive layer to the visible range of the spectrum.

In the circumstance that the organic photoconductor is a polymeric material which itself forms a film it is necessary to first put the sensitizers of this invention into solution. Understandably, the amount of the sensitizer that can be included in with a polymeric-type photoconductive system will be governed by the amount of material that can be put into solution.

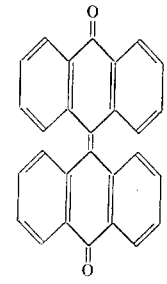
In systems where the photoconductive material is in monomeric form and is dispersed into a resin binder solution, the bianthrone derivatives may be added directly up to 100 percent based on the weight of the organic photoconductive material.

Chlorobenzene has been found to be a suitable solvent for the bianthrones and its derivatives permitting concentration of sensitizer up to 10 percent by weight of the organic photoconductor.

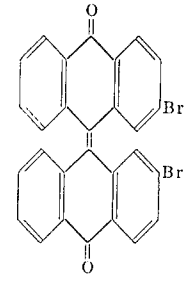
The preferred sensitizers are the halogen and hydrogen substituted bianthrone compounds. However, excellent sensitizing effects are obtained using the alkyl and fluoro derivatives.

The combination of ingredients is thoroughly mixed so that in the case of the polymeric photoconductive systems complete and uniform solution occurs. In the case of dispersion the materials are ball milled for a period of approximately 24 hours to obtain uniform blending of all ingredients. The mixture is then applied to a suitable substrate having the proper conductivity by such known techniques as a meniscus coater or trailing-blade coater, applying a thin film of the coating solution or dispersion to the surface. The solvent is then evaporated by forced air drying by passing the coating web through a heated oven. It has been found that best results are obtained by applying the coating formulations at a rate such that the sheet on a dry basis has a photoconductive layer in the range of 0.1–1.0 mil thick, the preferred thickness being in the range of 0.2–0.5 mil thick.

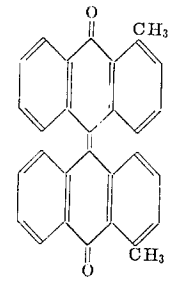
The methods of preparation of the compounds of this invention are known. The literature describes their preparation from dianthranol which when reacted with $FeCl_3$ and glacial acetic acid, alkaline $KMnO_4$, or Iodo potassium iodide is converted to bianthrone (Berichte 42,143–5). The following is a partial list of the compounds that can be used in carrying out this invention that come within the aforedescribed general formula:



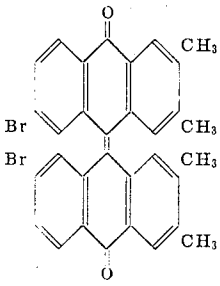
Bianthrone



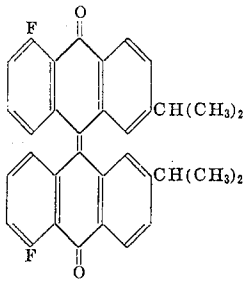
2,2′-dibromobianthrone



4,4′-dimethylbianthrone



7,7'dibromo-2,2',3,3'-tetramethylbianthrone



5,5-difluoro-2,2'-diisopropylbianthrone

EXAMPLE I

Polyvinylcarbazole	5 g.
Chlorobenzene	65 g.
Bianthrone	0.1 g.
Methylene chloride	35 g.

EXAMPLE II

Polyvinylcarbazole	5 g.
Chlorobenzene	65 g.
2,2'-Dibromobianthrone	0.3 g.
Methylene chloride	35 g.

EXAMPLE III

Polyvinylcarbazole	5 g.
Chlorobenzene	65 g.
Bianthrone	0.5 g.

EXAMPLE IV

Polyvinylcarbazole	5 g.
Chlorobenzene	65 g.
4,4'dibromomethylbianthrone	0.5 g.

EXAMPLE V

Polyvinylcarbazole	5 g.
Chlorobenzene	65 g.
7,7'Dibromo-2,2',3,3'-tetramethylbianthrone	1.0 g.

EXAMPLE VI

The coating formulation of this example is a dispersion of the photoconductive material in a resin binder. The crystals of 2,3' benzophenylene oxide are dispersed in a resin dissoved in a solvent and the sensitizer is then dispersed in the resin binder. The ingredients are balled milled for about 24 hours until the dispersion is uniform and applied to a suitable base support.

2,3'Benzodiphenylene oxide	10 g.
Polyvinyl formal resin	1 g.
Toulene	60 g.
Bianthrone	5 g.

EXAMPLE VIII

The coating formulation of this example is a dispersion type.

Chrysene	5 g.
Styrene-butadiene resin	5 g.
Toluene	50 g.
2,2'Dibromobianthrone	1.25 g.

EXAMPLE VIII

The coating formulation of this example is a dispersion type.

Triphenylene	1 g.
Styrene-butadiene resin	10 g.
Toluene	50 g.
Bianthrone	2 g.

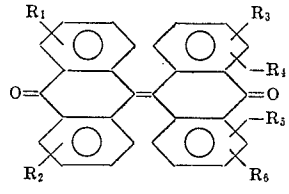
In each of the foregoing examples a photoresponse in the visible range was substantially increased over the formulations without the added sensitizer.

The photoelectrostatic members in each of the examples may be imaged by charging to a saturation voltage of 800 volts and then exposed to electromagnetic radiation in the visible range, such as is emitted by a Sylvania filament lamp contained in a quartz envelope rated at an intensity of 36 foot candles, which discharges the member to a level of 300 volts in a period ranging from 0.2–8 seconds. In the circumstance that the photoelectrostatic members of each of the examples prepared above had omitted therefrom the sensitizer, the time required to realize a voltage drop from a saturation level of 800 volts to the same level of 300 volts was in excess of 100 seconds.

The instant invention has been described in some detail reference being had to certain organic photoconductive materials. However, it will be readily apparent to those skilled in the art that the particular organic photoconductive material may be selected from the list of organic photoconductors disclosed herein which is only a partial list using either the monomeric form contained in an inert resin binder or a polymer capable of forming a continuous film when applied to a substrate and the effect of the sensitizers may be realized without limitation to the type of organic photoconductor employed.

What is claimed is:

1. A photoelectrostatic recording element comprising a conductive base coated with an aromatic organic photoconductor and a sensitizer having the formula



where R_1, R_2, R_3, R_4, R_5 and R_6 represent lower alkyl, halogen, and hydrogen substituents and R_1, R_2, R_3, R_4, R_5 and R_6 can be the same or different, said sensitizer being present in the range of 0.2 percent to 100 percent by weight based on the weight of organic photoconductor.

2. A photoelectrostatic member as claimed in claim 1 in which the sensitizer is bianthrone.

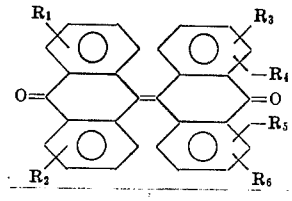
3. The photoelectrostatic member as claimed in claim 1 in which the sensitizer is 2,2'-Dibromobianthrone.

4. The photoelectrostatic member as claimed in claim 1 in which the sensitizer is 4,4'-Dimethylbianthrone.

5. The photoelectrostatic member as claimed in claim 1 in which the sensitizer is 7,7'dibromo-2,2'3,3'-tetramethylbianthrone.

6. The photoelectrostatic member as claimed in claim 1 in which the sensitizer is 5,5-difluoro-2,2'-diisopropylbianthrone.

7. The method of making a reproduction on a photoelectrostatic recording element comprising the steps of applying an electrostatic charge thereto, exposing to a pattern of light and shadow and then developing the differentially charged element by applying electroscopic particles thereto, said recording element comprising a conductive base support coated with an aromatic organic photoconductor and a sensitizer having the formula:



where R_1, R_2, R_3, R_4, R_5 and R_6 represent lower alkyl, halogen and hydrogen substituents and R_1, R_2, R_3, R_4, R_5 and R_6 can be the same or different, said sensitizer being present in the range of 0.2 percent to 100 percent by weight based on the weight of organic photoconductor.