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SUPERSENSITIZERS FOR OPTICALLY SENSITIZED PHOTOCONDUCTIVE LAYERS

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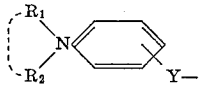
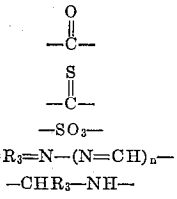
7 Claims. (Cl. 96—1.7)

ABSTRACT OF THE DISCLOSURE

The invention provides a superior class of supersensitizers for optically sensitized photoconductive layers, increasing their light sensitivity, which class of organic compounds have the radical



in which R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, alkaryl, and atoms necessary to form a heterocyclic ring having from 5 to 6 members; Y is a radical selected from the group consisting of



where R_3 is selected from the group consisting of hydrogen, alkyl, alkaryl and aryl; and n is selected from 0 and 1.

This invention relates to the optical sensitization of photoconductive materials and to methods of increasing the effectiveness of optical sensitizing dyes in photoconductive compositions useful in image recording. In one aspect this invention relates to additives which may be incorporated into photoconductive zinc oxide systems with optical sensitizers to produce a supersensitizing effect.

The optical sensitization of photoconductive materials has been described in the literature. Photoconductive copysheets used in electrolytic electrophotography, such as those described in U.S. Patent Nos. 3,010,883 and 3,010,884, are desirably sensitized to improve and extend their spectral response and efficiency. In another image recording process, i.e., electrostatic printing, such as described in U.S. Patent Nos. 3,052,539 and 3,052,540, the photoconductive sheets or coatings can also be dye sensitized. Because of the desirability of obtaining a white sheet color, the concentration of sensitizing dye is normally maintained at minimum levels consistent with improved spectral response.

Although the concept of supersensitization has been known in silver halide photography, it has not been possible merely to transfer such information, and materials over to photoconductive copysheets. Supersensitization may be considered as the increase in sensitivity which is obtained by the addition of certain materials, not necessarily sensitizers per se, to a sensitized system and which is not the result of a mere additive effect. In fact, supersensitization may be considered to be an exception to the general rule that the admixture of sensitizing dyes tends to reduce the overall sensitivity below that level provided by the respective components used individually. Though it is believed that supersensitization results from a mere efficient transfer of energy, in the form of excited

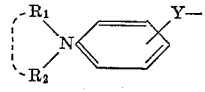
electrons, from the sensitizing dye to the zinc oxide conduction band, the actual mechanism is still not fully understood.

It is an object of this invention to provide supersensitizers for use in photoconductive systems, particularly in photoconductive recording elements.

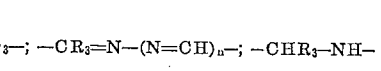
Another object of this invention is to provide increased speed of response in a photoconductive zinc oxide copysheet without objectionable sheet coloration.

Still another object of this invention is to provide photoconductive copysheets suitable for use in electrolytic electrophotography having increased speed and sensitivity without substantial increase in overall dark conductivity.

In accordance with this invention the above and other objects are achieved by incorporating into a dye sensitized photoconductive layer of a photoconductive copysheet an organic compound which is a complexing agent for zinc ion and which contains the radical



where R_1 and R_2 are hydrogen, alkyl (e.g., methyl, ethyl, butyl, hexyl, etc.), alkaryl (e.g., benzyl, etc.) or together form a 5 or 6 membered heterocyclic ring (e.g. morpholino, piperidino, piperazino, etc., and Y is



where R_3 is hydrogen, alkyl, alkaryl or aryl (including the substituted derivatives thereof) and n is 0 or 1.

Compounds such as N,N-dimethylaniline have essentially no supersensitizing value when used in conjunction with inorganic photoconductive materials (e.g., zinc oxide, cadmium sulfide, indium oxide, etc.), particularly as compared to the highly effective ring substituted anilines such as p-dimethylaminobenzaldehyde and p-dimethylaminobenzoic acid. The supersensitizers of this invention may generally be used in amounts ranging from about 0.0001% to about 1.5% by weight of the photoconductive material, preferably from 0.0001% to about 1.5% by weight. The preferred supersensitizers are not optical sensitizers per se for photoconductive zinc oxide.

The qualitative determination of the relative effectiveness of a compound as a supersensitizer can readily be accomplished by the following method. A dispersion is prepared by ball milling for several hours a mixture of 2867 grams of powdered zinc oxide (U.S.P. 12), 2821 grams of toluene, 100 milliliters of methanol and 2026 grams of a 30 weight percent solution of styrene-butadiene copolymer (30/70 mol ratio respectively) in toluene. The test compound is dissolved in a suitable solvent, e.g. methanol, to make a 2 weight percent solution, and 3.1 cubic centimeters of the resulting solution is added to 200 grams of the dispersion. After thorough mixing the sample is allowed to stand at room conditions for about 24 hours. A 3.5 milliliter quantity of the following sensitizing dye mixture is then added before coating:

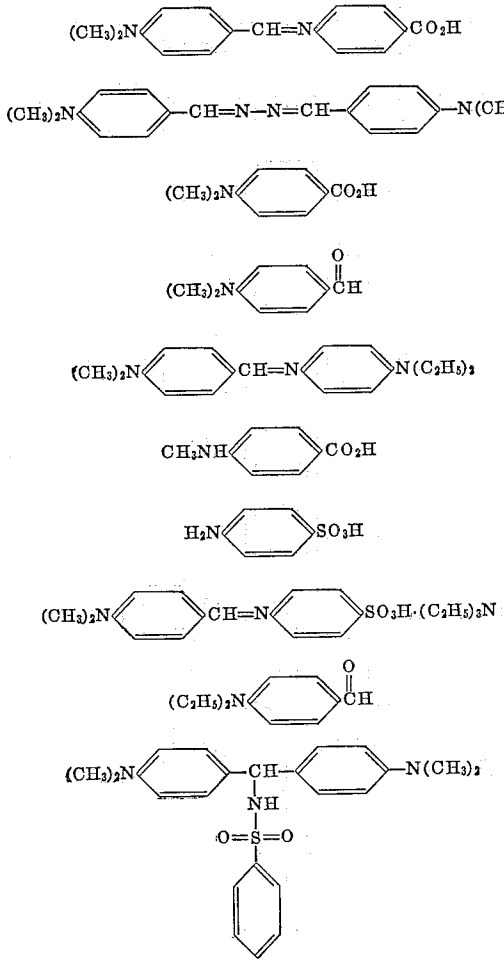
54 milliliters of 0.2 weight percent Sulfoflavine in methanol
27 milliliters of 0.2 weight percent Phloxine B (C.I. 42410) in methanol
19 milliliters of 0.5 weight percent Alphazurine 2G (C.I. 42045) in methanol

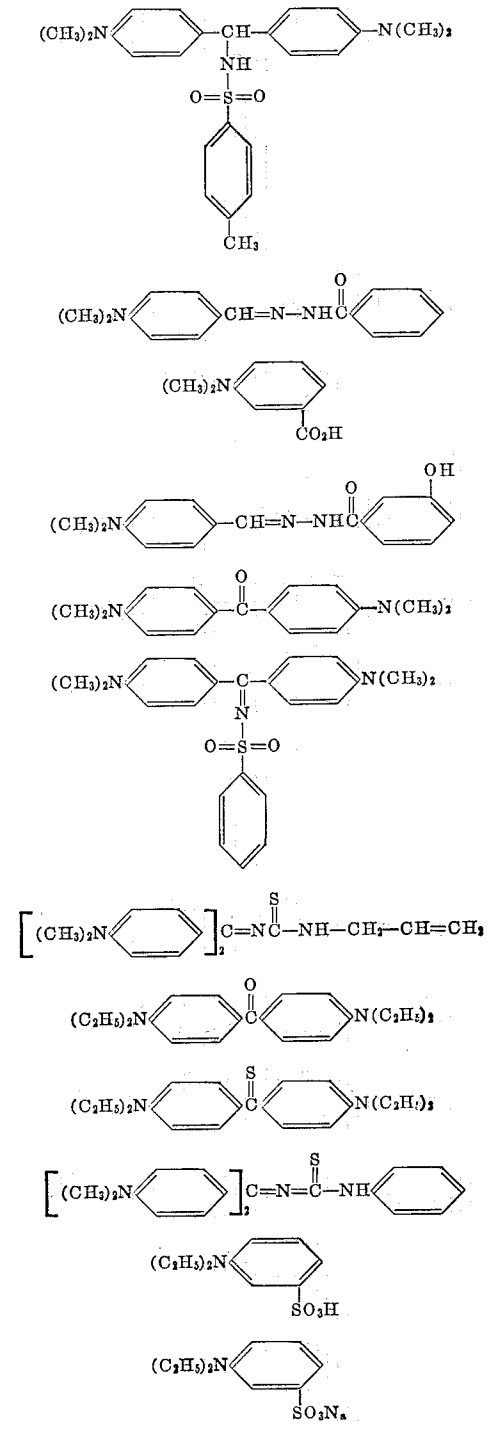
Other optical sensitizing dyes (e.g. cyanines, xanthenes, merocyanines, di- and tri-phenyl methanes) can be used, since the supersensitizers of this invention have not been

found to be specific to any specific optical sensitizer system. This dispersion is coated with a knife coater onto a suitable conductive substrate, such as an aluminum foil-paper laminate, to provide a dry coating thickness of about 0.7 mil. The coated substrate is then exposed with a standard light spectrogram source through a calibrated step wedge or a continuous grey wedge and electrolytically developed in a known manner. A control sample in which the test compound is omitted is prepared, exposed and electrolytically developed with the same procedure and under the same conditions. Visual examination and comparison of the developed samples will indicate whether the test compound performs a supersensitizing function in the photoconductive layer.

Illustrative examples of such ring substituted analine compounds, all of which exhibit at least a two-fold increase in sensitivity, are set forth in Table I. Using the testing method given above, sensitivity measurements were made at 4450, 5500 and 6500 angstroms. In general, the meta- and para-substituted anilines, particularly non-ionic para-substituted anilines are preferred. When acids are used, the corresponding salts, preferably the alkali or alkaline earth salts, may also be employed. The ability of the compound to form a complex with zinc ion can be determined in a conventional manner. Because of the enhanced sensitivity resulting from the use of such ring substituted analines, the amount of optical dye sensitizers included in the photoconductive layer along with the organic binder and photoconductor powder can be reduced, thereby improving sheet color. Essentially white or off-white copysheets are most desired in electrolytic electrophotography.

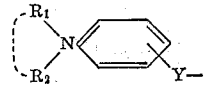
TABLE I





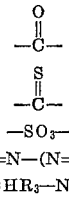
I claim:

1. In a light sensitive recording element having an optically sensitized photoconductive layer in which the photoconductive material is an inorganic photoconductor, the improvement which comprises from about 0.0001% to about 1.5% by weight of photoconductive material of a supersensitizer in said layer comprising a organic compound which is a complexing agent for zinc ion and which contains the radical



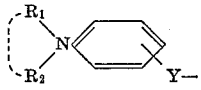
where R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, alkaryl, and atoms necessary to form

a heterocyclic ring having from 5 to 6 members; Y is a radical selected from the group consisting of

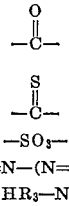


where R_3 is selected from the group consisting of hydrogen, alkyl, alkaryl and aryl; and *n* is selected from 0 and 1.

2. In a light sensitive recording element having an optically sensitized photoconductive zinc oxide layer and being suitable for use in electrolytic electrophotography, the improvement which comprises from about 0.0001% to about 1.5% by weight of zinc oxide of a supersensitizer in said layer comprising an organic compound which is a complexing agent for zinc ion and which contains the radical

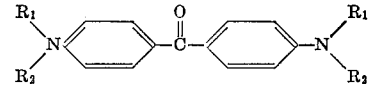


where R_1 and R_2 are selected from the group consisting of hydrogen, alkyl, alkaryl, and atoms necessary to form a heterocyclic ring having from 5 to 6 members; Y is a radical selected from the group consisting of



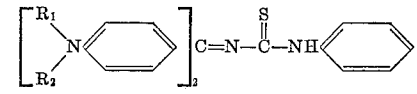
where R_3 is selected from the group consisting of hydrogen, alkyl, alkaryl and aryl; and *n* is selected from 0 and 1.

3. The light sensitive recording element of claim 2 in which said supersensitizer is



wherein R_1 and R_2 are as defined in claim 2.

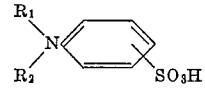
4. The light sensitive recording sheet of claim 2 in which said supersensitizer is



5. The light sensitive recording sheet of claim 2 in which said supersensitizer is p-dimethylamino benzaldehyde.

6. The light sensitive recording sheet of claim 2 in which said supersensitizer is m-dimethylamino benzoic acid.

7. The light sensitive recording sheet of claim 2 in which said supersensitizer is



or a salt thereof, where R_1 and R_2 are as defined in claim 2.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,352,670 November 14, 1967

Robert F. Coles

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 43, for "0.001%" read -- 0.0001% --.

Signed and sealed this 3rd day of December 1968.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents