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3,146,101

SENSITIZATION OF PHOTOCONDUCTIVE COPYSHEETS

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This invention relates to sensitizing photoconductive copysheets and a process for the preparation thereof. In one aspect, this invention relates to photoconductive zinc oxide copysheets having improved spectral sensitivity.

A recently developed image reproduction process involves electrolytically developing permanent and visible images on suitable, strongly photoconductive copysheets after exposure to light images. This method, described more fully in United States Patent Number 3,010,883, includes the electrolysis of an electrolytic developer and particularly the selective electrodeposition of a metallic or other visibly distinct coating at the exposed portions of the photosensitive surface, e.g. by electrolytic reduction. Strongly photoconductive copysheets suitable for the above method are described in United States Patent Number 3,010,884. To improve the sensitivity of such photoconductive copysheets various dye sensitizers, such as acridine orange, have been suggested. However, such dye sensitizers have frequently been strongly colored materials and have tended to discolor the surface of the photoconductive copysheets and detract from the quality of the image produced thereon. In certain instances, only extremely minute quantities of dye sensitizer could be tolerated because of discoloration. It has been desired, therefore, to find a sensitizing material which is relatively colorless and which can therefore be incorporated into a white photoconductive zinc oxide copysheet at higher levels of concentration to obtain improved spectral response.

It is therefore an object of this invention to provide strongly photoconductive copysheets having improved spectral response characteristics.

It is another object of this invention to provide a sensitized zinc oxide copysheet having relatively high concentration levels of optical sensitizer without substantially affecting the visual color of the copysheet.

It is still another object of this invention to provide a process for the preparation of photoconductive copysheets having improved spectral response.

In accordance with this invention photoconductive copysheets having enhanced spectral sensitivity are obtained by incorporating from about 1 to about 2,000 parts by weight of an amino coumarin compound per 40,000 parts by weight of photoconductive material in the photoconductive layer of the copysheet. The position of the amino group on the coumarin nucleus has not been found to be critical for sensitization, although variations in the sensitization can be expected depending on the particular amino coumarin selected. Similarly, the amino group can bear hydrogen, alkyl, alkaryl, or aryl substituents, or the amino nitrogen atom can constitute part of a heterocyclic ring, e.g. piperidine, morpholine, thiomorpholine, piperazine, etc. Illustrative amino coumarin compounds are 3-amino coumarin, 6-amino coumarin, 4-methyl-7-dimethylamino coumarin, 4-methyl-7-diethylamino coumarin, etc. The presence of at least one amino substituent on the coumarin nucleus is essential to obtain the desired sensitization, and amino-free coumarins, such as 3-methyl coumarin, 4-methyl-7-hydroxy coumarin and 6-methyl coumarin have displayed essentially no sensitizing effect on photoconductive zinc oxide. The preferred amino coumarin sensitizers are relatively colorless as visually observed in 0.1% solution in methyl ethyl ketone.

The amino coumarin compounds of this invention may be incorporated into the photoconductive portions of the copysheet in a variety of ways. It has been found to be particularly useful to add the amino coumarin in solution in an organic solvent, such as methyl ethyl ketone, to the mixture of photoconductive material and organic polymeric binder during the mixing thereof, preferably during the latter stages of the mixing operation. When the photoconductor and binder are ball milled for an extended period of time, it is preferable to avoid excessive ball milling in the presence of the amino coumarin sensitizer. When the photoconductor and binder material are mixed in the presence of a solvent, such as toluene and methyl ethyl ketone, the amino coumarin may be added directly to the mix as a dry powder and the resultant admixture blended. As mentioned earlier, from 1 to 2,000 parts by weight of the amino coumarin, preferably from 10 to about 1,000 parts by weight, per 40,000 parts by weight of photoconductive material is employed. Zinc oxide is preferred as the photoconductive material and is particularly desirable for the preparation of a white copysheet. The sensitized admixture of photoconductor and binder in an organic solvent is then coated onto a clean electrically conductive backing, e.g. aluminum foil or laminate, as more fully described in United States Patent Number 3,010,884.

The increased sensitivity observed with the use of the amino coumarin derivatives of this invention is most particularly evident in the blue region of the light spectrum, especially at about 425 angstroms. Since the sensitizing effect appears to be additive, i.e. a red sensitizer used in conjunction with the amino coumarin tends to provide a photoconductive coating with enhanced sensitivity to both red and blue light, other sensitizers and supersensitizers can be used in conjunction with these coumarin derivatives. Moreover, since the amino coumarin sensitizers do not tend to adversely discolor the photoconductive coating, a desirably whiter copysheet can be prepared.

The following examples will illustrate the invention and are not intended to restrict the scope thereof.

Example I

An admixture containing 42 weight percent of French process zinc oxide powder (U.S.P. 12), 35 weight percent of a 30% solution of butadiene-styrene copolymer (30:70 mol ratio) in toluene, and 23 weight percent of methyl ethyl ketone, was ball milled in a pint jar with porcelain balls for four hours and coated onto the aluminum surface of aluminum laminate paper. The coating was made with a 4-mil wet coating thickness. A second mix was prepared in similar manner, with the addition of 0.042 gram of 4-methyl-7-diethylamino coumarin per 100 grams of mix before the end of the ball milling operation. This second mix was similarly coated onto aluminum laminate. Using a 35 mm. slide containing gray scales and primary color filters in a 200 watt incandescent light projector (*f*3.5, 50 mm. lens) and an enlargement to 5.5 x 8 inches, sensitivity tests were conducted on both coated samples. After standard exposures, the samples were cathodically electrolyzed by sponging with an anode containing sponge holding an aqueous solution of 10% $NiCl_2 \cdot 6H_2O$ and 5% $Na_2S_2O_3$, thereby developing a dark nickel image on the light struck areas. A marked increase in sensitivity to blue and white light was observed in the second sample containing the amino coumarin sensitizer compared to the first sample.

Example II

The procedure of Example I was repeated, using 1 gram of 4-methyl-7-dimethylamino coumarin per 100

grams of mix. An even greater improvement in the sensitivity to blue and white light than obtained in Example I was observed. The use of 4-methyl-7-hydroxy coumarin instead of 4-methyl-7-diethylamino coumarin did not produce any significanct increase in sensitivity to blue and white light.

Example III

Following the same procedure as in Example II, 1 gram of 4-methyl-7-dimethylamino coumarin was added per 100 grams of mix. Significant increase in sensitivity to blue and white light was noted. Neither 6-methyl coumarin nor 3-methyl coumarin showed any significant improvement in white light sensitivity.

Example IV

Using the same procedure as in Example II, 1 gram of 6-amino coumarin was added per 100 grams of mix. The sensitivity to blue and white light was markedly increased. 3-amino coumarin also provided improved sensitivity in the blue portion of the light spectrum.

Various other embodiments of the present invention will be apparent to those skilled in the art without departing from the scope thereof.

I claim:

1. In a copysheet having a photoconductive zinc oxide therein the improvement which comprises from about 1 to about 2,000 parts by weight of an amino coumarin per 40,000 parts of said photoconductor, said amino coumarin being intimately admixed with said photoconductor.

2. In a copysheet having a photoconductive zinc oxide layer the improvement which comprises an amino coumarin in said photoconductive layer in a quantity sufficient to increase the sensitivity thereof.

3. In a copysheet having a photoconductive zinc oxide layer the improvement which comprises 4-methyl-7-diethylamino coumarin in said photoconductive layer in a quantity sufficient to increase the blue light sensitivity thereof.

4. In a copysheet having a photoconductive zinc oxide layer the improvement which comprises 4-methyl-7-dimethylamino coumarin in said photoconductive layer in a quantity sufficient to increase the blue light sensitivity thereof.

5. In a copysheet having a photoconductive zinc oxide layer the improvement which comprises 6-amino coumarin in said photoconductive layer in a quantity sufficient to increase the blue light sensitivity thereof.

6. In a copysheet having a photoconductive zinc oxide layer the improvement which comprises 3-amino-coumarin in said photoconductive layer in a quantity sufficient to increase the blue light sensitivity thereof.

7. A photoconductive copysheet having a layer comprising photoconductive zinc oxide material and, intimately admixed therewith, an amino coumarin as a sensitizer.

8. A photoconductive zinc oxide copysheet having a light sensitive layer comprising a photoconductive powder and, in intimate association therewith, between about 1 and about 2,000 parts by weight of an amino coumarin sensitizer per 40,000 parts of said photoconductive powder.

9. The photoconductive copysheet of claim 8 wherein the amount of said amino coumarin sensitizer is insufficient to substantially alter the visual color of the copysheet.

10. A photoconductive copysheet having an electrically conductive substrate and a light sensitive layer comprising a photoconductive zinc oxide powder and, in intimate association therewith, an amino-coumarin in a quantity sufficient to increase the blue light sensitivity thereof without substantially altering the color of said light sensitive layer.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,146,101 August 25, 1964

Byron W. Neher

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 4, line 13, strike out "zinc oxide" and insert the same after "photoconductive", in line 14, same column 4.

Signed and sealed this 5th day of January 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents