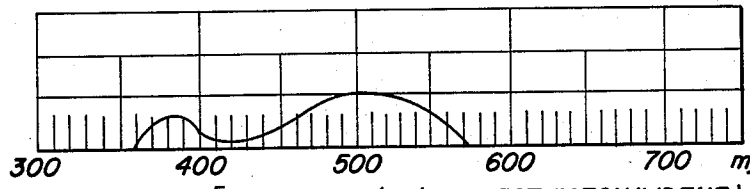
Nov. 12, 1963 P. H. STEWART 3,110,591

MEROCYANINE SENSITIZED PHOTOCONDUCTIVE COMPOSITIONS COMPRISING ZINC OXIDE

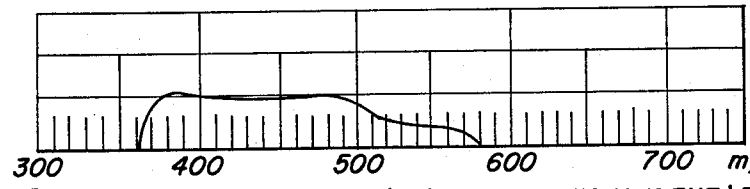
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Fig. 1



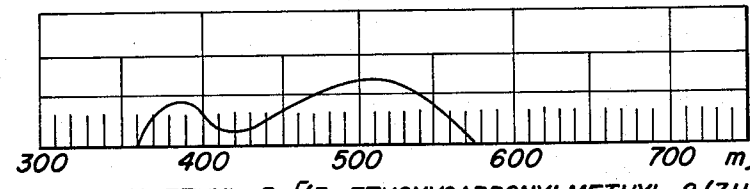
3-CARBOXY-4-[(3-ETHYL-2(3H)-BENZOTHIAZOLYLIDENE) ETHYLIDENE]-5-PYRAZOLONE

Fig. 2



5-[(5-CARBOXY-3-METHYL-2(3H)-BENZOXAZOLYLIDENE) ETHYLIDENE]-2,4-THIAZOLIDINEDIONE

Fig. 3



3-CARBOXYMETHYL-5-[(3-ETHOXYCARBONYLMETHYL-2(3H)-THIAZOLINYLIDENE) ISOPROPYLIDENE] RHODANINE

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United States Patent Office

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MEROCYANINE SENSITIZED PHOTOCONDUCTIVE COMPOSITIONS COMPRISING ZINC OXIDE

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Filed Apr. 22, 1960, Ser. No. 24,122
11 Claims. (Cl. 96—1)

This invention relates to optically sensitized photoconductive layers comprising zinc oxide which are particularly useful in making photographic copies (black and white, or color), and a method of making such photoconductive compositions.

This application is a continuation-in-part of my application Serial No. 630,462, filed December 26, 1956, now abandoned.

It is known that zinc oxide can be employed in making photoconductive layers on ordinary paper and that photographic copies can conveniently be prepared from these photoconductive papers. This process has been described as being somewhat similar to the system known as xerography in that a photoconductive plate is employed and after exposure of the plate to a photographic image, development of the latent image is accomplished by means of a pigmented resinous composition which adheres to the unexposed portions of the exposed plate. However, the xerographic plate is generally used to transfer the developed image to a receiving sheet, whereas the known system for using photoconductive zinc oxide generally makes use of the zinc oxide layer itself as a means of providing the desired photographic copy without transfer of any electrostatic charge to a receiving sheet.

In the known system of employing zinc oxide in photoconductive layers, the grounded support, which is generally paper, is first made sensitive to light by giving it a blanket negative electrostatic charge on the zinc oxide layer in the substantial absence of any ultraviolet or visible radiation. One convenient means of giving the zinc oxide layer an electrostatic negative charge is by means of ion transfer from a corona discharge. The zinc oxide photoconductive layer can then be exposed to a photographic image in the usual manner, the portions of the zinc oxide which receive light or ultraviolet radiation losing wholly, or in part (depending upon extent of exposure), the negative electrostatic charge, while the unexposed portions of the photoconductive layer retain their negative electrostatic charge. The resulting latent image can then be developed by means of a pigmented resin powder which has a charge opposite to the negative charge of the unexposed areas of the photoconductive layer. The pigmented powder is thus firmly attached or attracted to the negatively charged areas. The pigmented resin powder can then be affixed to the photoconductive layer by simply melting the resinous vehicle at a temperature below the charring temperature of the paper support, so that the resinous powder becomes fused to the surface of the original photoconductive layer. Various means of developing the latent image in the photoconductive layer to a visible image have been described in the prior art.

One disadvantage in the zinc oxide normally used in such photoconductive layers is that the light-sensitivity of such charged zinc oxide normally is at its greatest in the ultraviolet region of the spectrum, whereas the exposing source may have its maximum output in a region

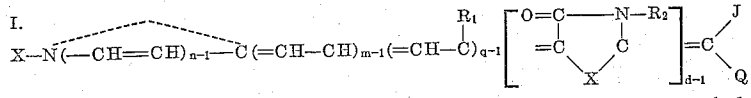
of the spectrum which lies within the visible region, such as an ordinary tungsten light. While various means have been previously described for sensitizing the zinc oxide so that it has some panchromatic or orthochromatic sensitivity, for example, by means of various organic dyes such as Rose Bengal, and the like, these methods have not been particularly satisfactory since the disadvantage of strongly dyeing the zinc oxide layer more than offsets the sensitivity which is supplied to the feebly sensitive zinc oxide. That is, it is generally desirable to have some means of sensitizing the zinc oxide which does not permanently color the zinc oxide layer, which might be used as the final copy of the photographic image. Strong coloration of the zinc oxide layer has an unfavorable aesthetic effect and might be strongly objectionable in the event that it is desired to make color prints of the original subject. Other unfavorable effects, such as poor contrast, slow speeds, etc., are evident.

It is an object of my invention to provide a convenient means of optically sensitizing zinc oxide photoconductive layers in a useful manner. Another object is to provide a means of optically sensitizing zinc oxide photoconductive layers by means of merocyanine dyes. Still another object is to provide a particular class of merocyanine dyes which are outstanding in their optical sensitizing properties for zinc oxide photoconductive layers. Other objects will become apparent from a consideration of the following description and examples.

My invention is illustrated graphically in the accompanying drawing where FIGURES 1–3 are spectograms of zinc oxide compositions sensitized according to my invention.

The merocyanine or polymethine dyes which can be used in practicing my invention comprise dyes known in the art as simple merocyanine dyes, merocarbocyanine dyes, merodicarbocyanine dyes, complex merocyanine dyes and "open-chain" merocyanine dyes, provided such dyes contain at least one carboxyl group. The carboxyl group can be attached directly to the molecule of the parent or carboxyl-free dyes, or the carboxyl group can be attached to the molecule through an alkyl or aryl group. The merocyanine or polymethine dyes useful in practicing my invention include those dyes represented by the following general formula:

I.



wherein R represents an alkyl group (e.g., methyl, ethyl, n-propyl, n-butyl, isobutyl, n-amyl, isoamyl, etc.), a hydroxyalkyl group (e.g., β-hydroxyethyl, γ-hydroxypropyl, etc.), an alkoxyalkyl group (e.g., β-methoxyethyl, β-ethoxyethyl, etc.), a carboxyalkyl group (e.g., carboxymethyl, β-carboxyethyl, α-carboxyethyl, γ-carboxypropyl, etc.), a sulfoalkyl group (e.g., sulfomethyl, β-sulfoethyl, γ-sulfopropyl, δ-sulfobutyl, etc.), a carbalkoxyalkyl group (e.g., carbomethoxymethyl, β-carbomethoxyethyl, carbethoxymethyl, β-carbethoxyethyl, etc.), an acyloxyalkyl group (e.g., β-acetoxyethyl, γ-acetoxypropyl, etc.), an aralkyl group (e.g., benzyl, β-phenethyl, etc.), etc., R_1 represents a hydrogen atom, an alkyl group (e.g., methyl, ethyl, etc.), or an aryl group (e.g., phenyl, tolyl, etc., especially a monocyclic aryl group of the benzene series), R_2 represents a hydrogen atom, an alkyl group (e.g., methyl, ethyl, n-propyl, n-amyl, n-heptyl, etc.), a hydroxyalkyl group (e.g., β-hydroxyethyl, γ-hydroxypropyl, etc.), a carbalkoxyalkyl group (e.g., carbethoxymethyl, β-carbethoxyethyl, etc.), a carboxyalkyl group (e.g., carboxymethyl, β-carboxyethyl, α-carboxyethyl, γ-carboxypropyl, δ-carboxybutyl, etc.), or an aryl group (e.g., phenyl, tolyl, carboxyphenyl, sulfophenyl, etc., especially

a monocyclic aryl group of the benzene series), X represents an oxygen atom, a sulfur atom or a NR' group wherein R' represents an alkyl group (e.g., methyl, ethyl, etc.) or an aryl group (e.g., phenyl, tolyl, etc., especially a monocyclic aryl group of the benzene series), *d*, *n* and *q* each represents a positive integer of from 1 to 2, *m* represents a positive integer of from 1 to 3, Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, J represents a cyano group when Q represents a cyano group or a carbalkoxyl group (e.g., carbomethoxyl, carboethoxyl, carbobutoxyl, etc., especially such groups containing from 2 to 5 carbon atoms), or J and Q together can represent the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, which nuclei have a carbonyl group attached to the carbon atom to which J and Q are attached in the formula shown above, provided d is one when J represents a cyano group and Q represents a cyano group or a carbalkoxyl group.

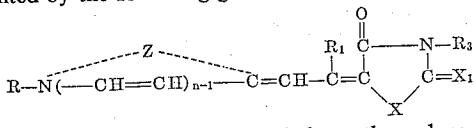
Typical heterocyclic nuclei as defined by Z above include those of the thiazole series (e.g., thiazole, 4-methylthiazole, 5-methylthiazole, 4-phenylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.), those of the benzothiazole series (e.g., benzothiazole 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzotihazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 6-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5 - methoxybenzothiazole, 6 - methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6 - dimethoxybenzothiazole, 5,6 - dioxymethylenebenzothiazole, 5 - hydroxybenzothiazole, 6 - hydroxybenzothiazole, 5 - carboxybenzothiazole, etc.), those of the naphthothiazole series (e.g., α-naphthothiazole, β-naphthothiazole, 5-methoxy-β-naphthothiazole, 5-ethoxy-β-naphthothiazole, 7-methoxy-α-naphthothiazole, 8-methoxy-α-naphthothiazole, etc.), those of the thianaphtheno-7',6',4,5-thiazole series (e.g., 4'-methoxythianaphtheno-7', 6', 4,5-thiazole, etc.), those of the oxazole series (e.g., 4-methyloxazole, 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.), those of the benzoxazole series (e.g., benzoxazole, 5-chlorobenzoxazole, 5-phenylbenzoxazole, 5-methylbenzoxazole, 6-methylbenzoxazole, 5,6 - dimethylbenzoxazole, 4,6 - dimethylbenzoxazole, 5-methoxybenzoxazole, 6 - methoxybenzoxazole, 5-ethoxybenzoxazole, 6-chlorobenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, 5-carboxybenzoxazole, etc.), those of the naphthoxazole series (e.g., α-naphthoxazole, β-naphthoxazole, etc.), those of the selenazole series (e.g., 4-methylselenazole, 4-phenylselenazole, etc.), those of the benzoselenazole series (e.g., benzoselenazole, 5-chlorobenzoselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.), those of the naphthoselenazole series (e.g., α-naphthoselenazole, β-naphthoselenazole, etc.), those of the thiazoline series (e.g., thiazoline, 4-methylthiazoline, etc.), those of the 2-quinoline series (e.g., quinoline 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc.), those of the 4-quinoline series (e.g., quinoline, 6-methoxyquinoline, 7-methylquinoline, 8-methylquinoline, etc.), those of the 1-isoquinoline series (e.g., isoquinoline, 3,4-dihydroisoquinoline, etc.), those of the 3,3-dialkylindolenine series (e.g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,3,7-trimethylindolenine, etc.), those of the 2-pyridine series (e.g., pyridine, 3-methylpyridine, 4-methylpyridine, 5-methylpyridine, 6-methylpyridine, 3,4-dimethylpyridine, 3,5-dimethylpyridine, 3,6-dimethylpyridine, 4,5-dimethylpyridine, 4,6-dimethylpyridine, 4-chloropyridine, 5-chloropyrdine, 6-chloropyridine, 3-hydroxypyridine, 4 - hydroxypyridine, 5 - hydroxypyridine, 6-hydroxypyridine, 3-phenylpyridine, 4-phenylpyridine, 6-phenylpyridine, etc.), those of the 4-pyridine series (e.g., 2-methylpyridine, 3-methylpyridine, 2-chloropyridine, 3-chloropyridine, 2,3-dimethylpyridine, 2,5-dimethylpyridine, 2,6-dimethylpyridine, 2-hydroxypyridine, 3-hydroxypyridine, etc.), etc.

Heterocyclic nuclei formed by the combination of J and Q of Formula I above comprise heterocyclic nuclei containing from 5 to 6 atoms in the heterocyclic ring, such as those of the pyrazolone series (e.g., 3-methyl-1-phenyl-5-pyrazolone, 1-phenyl-5-pyrazolone, 1-(2-benzothiazolyl)-3-methyl-5-pyrazolone, etc.), those of the isoxazolone series (e.g., 3-phenyl-5-(4H)-isoxazolone, 3-methyl-5-(4H)-isoxazolone, etc), those of the oxindole series (e.g., 1-alkyl-2,3-dihydro-2-oxindoles, etc.), those of the 2,4,6-triketo- or 2-thio-4,6-diketohexahydropyrimidine series (e.g., barbituric acid or 2-thiobarbituric acid as well as their 1-alkyl (e.g., 1-methyl, 1-ethyl, 1-n-propyl, 1-n-heptyl, etc.) or 1,3-dialkyl (e.g., 1,3-dimethyl, 1,3-diethyl, 1,3-di-n-propyl, 1,3-diisopropyl, 1,3-dicyclohexyl, 1,3-di(β-methoxyethyl), etc.), or 1,3-diaryl (e.g., 1,3-diphenyl, 1,3-di(p-chlorophenyl), 1,3-di(p-ethoxycarbonylphenyl), etc.), or 1-aryl (e.g., 1-phenyl, 1-p-chlorophenyl, 1-p-ethoxycarbonylphenyl), etc.) or 1-alkyl-3-aryl (e.g., 1-ethyl-3-phenyl, 1-n-heptyl-3-phenyl, etc.) derivatives), those of the rhodanine series (i.e. 2-thio-2,4-thiazolidinedione series), such as rhodanine, 3-alkylrhodanines (e.g., 3-ethylrhodanine, 3 - allyl - rhodanine, etc.), or 3-arylrhodanines (e.g., 3-phenylrhodanine, etc.), etc., those of the 2(3H) - imidazo[1,2 - a]pyridone series, those of the 5,7-dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine series (e.g., 5,7-dioxo-3-phenyl-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine, etc.), those of the 2-thio-2,4-oxazolidinedione series (i.e., those of the 2-thio-2,4(3H, 5H)-oxazoledione series) (e.g. 3-ethyl-2-thio-2,4-oxazolidinedione, etc.), those of the thianaphthenone series (e.g., 3(2H)-thianaphthenone, etc.), those of the 2-thio-2,5-thiazolidinedione series (i.e., the 2-thio-2,5(3H,4H)-thiazoledione series) (e.g., 3-ethyl-2-thio-2,5-thiazolidinedione, etc.), those of the 2,4-thiazolidinedione series (e.g., 2,4-thiazolidinedione, 3-ethyl-2,4-thiazolidinedione, 3-phenyl - 2,4 - thiazolidinedione, 3-α-naphthyl-2,4-thiazolidinedione, etc.), those of the thiazolidinone series (e.g., 4-thiazolidinone, 3 - ethyl - 4 - thiazolidinone, 3-phenyl-4-thiazolidinone, 3-α-naphthyl-4-thiazolidinone, etc.), those of the 4-thiazolinone series (e.g., 2-ethylmercapto-4-thiazolinone, 2-alkylphenylamino-4-thiazolinones, 2-diphenylamino-4-thiazolinone, etc.), those of the 2-imino-2,4-oxazolinone (i.e., pseudohydantoin) series, those of the 2,4-imidazolinedione (hydantoin) series (e.g., 2,4-imidazolinedione, 3-ethyl-2,4-imidazolinedione, 3-phenyl-2,4-imidazolinedione, 3-α-naphthyl-2,4-imidazolinedione, 1,3-diethyl-2,4-imidazolinedione, 1-ethyl-3-α-naphthyl-2,4-imidazolinedione, 1,3-diphenyl-2,4-imidazolinedione, etc.), those of the 2-thio-2,4-imidazolinedione (i.e., 2-thiohydantoin) series (e.g., 2-thio-2,4-imidazolinedione, 3-ethyl-2-thio-2,4-imidazolinedione, 3-phenyl-2-thio-2,4-imidazolinedione, 3-α-naphthyl-2-thio-2,4-imidazolinedione, 1,3-diethyl - 2 - thio-2,4-imidazolinedione, 1-ethyl-3-phenyl-2-thio,2,4-imidazolinedione, 1-ethyl-3-α-naphthyl-2-thio-2,4-imidazolinedione, 1,3 - diphenyl - 2-thio-2,4-imidazolinedione, etc.), those of the 5-imidazolinone series (e.g., 2-n-propylmercapto-5-imidazolinone, etc.), as well as heterocyclic nuclei containing a sulfone group, such as those described in U.S. Patent 2,748,114 (e.g., 4-thiazolidone-1,1 - dioxide, 3(2H)-thianaphthenone-1,1-dioxide, etc.) (especially a heterocyclic nucleus containing 5 atoms in the heterocyclic ring, 3 of said atoms being carbon atoms, 1 of said atoms being a nitrogen atom, and 1 of said atoms being selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom). Of course, it is to be understood that the dyes useful in my invention contain at least one free carboxyl group attached to a carbon atom of the dyes depicted by Formula I.

The carboxyl-substituted dyes of my invention are markedly superior to the carboxyl-free dyes, as hereinafter shown. Dyes containing a carboxyethyl group have been found to be particularly useful.

Among the most useful dyes in practicing my invention are merocarbocyanine dyes containing at least one free carboxyl group. These dyes can advantageously be represented by the following general formula:

II.



wherein R, R_1, n, Z and X each have the values given above, X_1 represents an oxygen atom or a sulfur atom and R_3 represents an alkyl or substituted alkyl group, such as those listed above under R, or alternatively R_3 represents an aryl group (e.g., phenyl, tolyl, etc.). Particularly useful dyes include those wherein R_3 represents a carboxyalkyl or carboxyaryl group (e.g., carboxymethyl, β-carboxyethyl, carboxybutyl, o-, m- or p-carboxyphenyl, etc.). Many of these merocarbocyanine dyes have excellent sensitizing action in the green and/or red regions of the spectrum.

Merocyanine or polymethine dyes useful in practicing my invention include the following:

(1) 3 - carboxymethyl - 5 - (3 - ethyl - 2(3H) - benzothiazolylidene)-rhodanine

(2) 3 - β - carboxyethyl - 2 - (3,3 - dicyanoallylidene) benzothiazoline

(3) 3 - carboxymethyl - 2 - (3,3 - dicyanoallylidene) benzothiazoline

(4) 3 - carboxymethyl - 5 - [(3 - methyl - 2(3H) - thiazolinylidene)isopropylidene]rhodanine

(5) 3 - ethyl - 5 - [(3 - carboxymethyl - 2(3H) - benzoxazolylidene)-ethylidene]rhodanine

(6) 3 - carboxymethyl - 5 - [(3 - ethyl - 2(3H) - benzoxazolylidene)-ethylidene]rhodanine

(7) 3 - carboxymethyl - 5 - [(3 - ethyl - 2(3H) - benzothiazolylidene)-ethylidene]rhodanine

(8) 2 - (3 - carboxymethyl - 4 - oxo - 2 - thiono - 5-thiazolidylidene)-3-ethyl-5-[(3-ethyl-2(3H)-benzoxazolylidene)ethylidene]-4-thiazolidone

(9) 3 - carboxy - 4 - [(3 - ethyl - 2(3H) - benzothiazolylidene)-ethylidene]-5-pyrazolone

(10) 5-[(3-β-carboxyethyl-2(3H)-benzoxazolylidene)-2,4-hexadienylidene]-1,3-diphenylbarbituric acid

(11) 4-[3-carboxyethyl-2-(3H)-benzoxazolylidene) butenylidene]-3-phenyl-2-isoxazolin-5-one

(12) 4-[(3-carboxyethyl-2(3H)-benzoxazolylidene)-2,4-hexadienylidene]-3-phenyl-2-isoxazolin-5-one

(13) 4-[(3-β-carboxyethyl-2(3H)-benzoxazolylidene) ethylidene]-3-phenyl-2-isoxazolin-5-one

(14) 1-carboxymethyl-5-[(3-ethyl-2(3H)-benzoxazolylidene)-ethylidene-3-phenyl-2-thiobarbituric acid

(15) 3-carboxymethyl-5-(1-methyl-2(1H)-pyridylidene) rhodanine

(16) 3-carboxymethyl-5-[(3-ethoxycarbonylmethyl-2(3H)-thiazolinylidene)isopropylidene]rhodanine

(17) 5-[(3-carboxyethyl-2-(3H)-thiazolinylidene)ethylidene]-3-carboxymethylrhodanine

(18) 5-(1β-carboxyethyl-4(1H)-pyridylidene)-3-ethylrhodanine

(19) 2-(3-carboxymethyl-4-oxo-2-thio-5-thiazolidinylidene)-3-ethyl-5[(1-ethyl-2(1H)-naphtho[1,2]thiazolylidene)-1-phenylethylidene]-4-thiazolidinone

(20) 5-[(5-carboxy-3-methyl-2(3H)-benzoxazolylidene) ethylidene]-2,4-thiazolidinedione

(21) 5-[3-β-carboxyethyl-2(3H)-benzothiazolylidene) ethylidene]-2,4-thiazolidinedione

(22) 5-[1-o-carboxyphenyl-2-(3-ethyl-2(3H)-benzothiazolylidene)ethylidene]-3-ethylrhodanine

(23) 5-[3-o-carboxyphenyl-4-(3-ethyl-2(3H)-benzothiazolylidene)-but-3-enylidene]-3-ethoxycarbonylmethylrhodanine

(24) 5-[1-o-carboxyphenyl-2-(5-chloro-3-ethyl-2-(3H)-benzothiazolylidene)ethylidene]-3-ethoxycarbonylmethylrhodanine

(25) 5-[1-o-carboxyphenyl-2-(3-ethyl-2(3H)-benzothiazolylidene)ethylidene]-3-ethoxycarbonylmethylrhodanine

(26) 5-[(1-(4-carboxybutyl)-5,6-dichloro-3-ethyl-2(3H)-benzimidazolylidene)ethylidene]-3-ethylrhodanine

Methods for making the above merocyanine or polymethine dyes have been previously described in the prior art. Among the patents describing the preparation of such dyes are the following:

U.S. 2,493,747 issued on January 10, 1950
U.S. 2,493,748 issued on January 10, 1950
U.S. 2,519,001 issued on August 15, 1950
U.S. 2,526,632 issued on October 24, 1950
U.S. 2,778,822 issued on January 22, 1957
British 450,958 issued on July 15, 1936

Other patents showing such dyes include Knott U.S. Patent 2,728,766, issued December 27, 1955 and Brooker U.S. Patent 2,454,629, issued November 23, 1948. Merocyanine dyes containing a carboxyl group attached to the benzene ring of a heterocyclic nucleus can be prepared by reacting the carboxyl-substituted cyclammonium quaternary salts of Firestine U.S. Patents 2,609,371, issued September 2, 1952 and 2,647,057, issued July 28, 1953, with a Dains et al. type intermediate according to methods well known to those skilled in the art.

The above optical sensitizing dyes can be combined with the zinc oxide photoconductive material in any convenient manner. For example, the optical sensitizing dye can be added to the zinc oxide composition while dissolved in an organic solvent. Pyridine, methanol, ethanol, acetone, etc., can be used to dissolve many of the merocyanine dyes useful in practicing my invention. The zinc oxide can be uniformly dispersed in an organic solution of the binder customarily employed for the zinc oxide and a solution of the merocyanine dye added to this coating solution. After thorough mixing, the sensitized solution can be coated on a paper support and dried in the usual manner.

Alternatively, an unsensitized zinc oxide coating can be prepared as described above and after removal of the organic solvent, the paper coating can be immersed in a solution (organic or aqueous) of the merocyanine dye. This method has been found to be particularly useful in that higher speeds can be frequently obtained.

The binders for the zinc oxide comprise many of the resinous compositions which are commercially available. Such resins are sold under trade names, such as Plaskon ST 856, Rezyl 405–18, Pliolite S–7, Styresol 4440, DC 804, etc. These resins comprise styrene-butadiene copolymers, silicone resins, styrene-alkyd resins, silicone-alkyd resins, soya-alkyd resins, polyvinyl chloride, polyvinyl acetate, etc. The methods of making such resins have been previously described in the prior art. For example, styrene-alkyd resins can be prepared according to the method described in U.S. Patent 2,361,019, issued October 24, 1944; U.S. Patent 2,258,423, issued October 7, 1941; U.S. Patent 2,453,665, issued November 9, 1948, etc. Other binders, such as paraffin, mineral waxes, etc., can also be employed. These binders are generally characterized as having marked hydrophobic properties (i.e., being substantially free of any water-solubilizing groups, such as hydroxyl, free acid groups, amide groups, etc.) and as being good electrical insulators or as having high electrical resistivity. These binders can be easily dissolved in organic solvents having a boiling point below the charring temperature of the paper support. Also, these binders have the desirable property of readily dispersing the zinc oxide photoconductive material. Some resinous binders are relatively poor insulators and do not provide coatings which can be stored for prolonged periods of

times after the photoconductive coatings have been negatively charged. This is particularly noticeable at relatively high humidities, and the photoconductive coatings should be negatively charged shortly before use in such instances, that is, it is not advisable to charge the photoconductive coatings too long in advance before use. Such problems are well understood by those skilled in the art.

Nonpolar solvents have been found to be particularly useful in preparing the photoconductive layers in that any residual solvent which cannot be removed does not have a deleterious effect on the keeping qualities of the photoconductive layers. Such solvents include the aromatic hydrocarbons, such as benzene, xylenes, toluene, etc.

The zinc oxide photoconductive material employed in my invention should generally consist of relatively small particles of less than 0.5 micron mean diameter. Such zinc oxide materials are readily available and can be purchased under a variety of trade names, such as Protox No. 168 (New Jersey Zinc Company), etc. Sufficient binder should be employed to insulate each of the zinc oxide particles from the surrounding particles in the composition. The most useful or optimum quantity of zinc oxide to binder for a particular binder can be readily determined by making a series of test coatings wherein the quantity and relative amounts of zinc oxide to binder are employed.

Exposure of the charged photoconductive layer to visible radiation or ultraviolet radiation causes a loss or reduction of the negative charge in those portions of the photo-conductive material which are exposed to the radiation. The degree of loss will depend on the intensity and time of exposure to the radiation, in general. The resulting latent electrophotographic image can then be developed to a visible image in a variety of ways, including those which have been previously employed in electrophotographic processes, such as xerography. A particularly useful means of developing the latent electrophotographic image comprises use of a magnetic brush. This magnetic brush development makes use of a ferromagnetic powder, such as iron filings, which has been intimately mixed with pigmented resin, or sulfur. Agitation of the ferromagnetic powder and pigmented resin results in a triboelectric effect wherein the pigmented resin acquires an electric charge depending upon the relative position of the resin to the ferromagnetic powder in the triboelectric series. That is, ordinary iron powder is below most resins in the triboelectric series, and mixture with a resin higher in the series results in the deposition of a positive electrostatic charge on the resin. The resulting mixture can then be picked up by a magnet on which the iron particles, or other ferromagnetic powder, arrange themselves in the conventional pattern, so that the long chains of filings resemble an ordinary brush. This magnetic brush can then be placed in contact with the exposed photoconductive layer and the brush passed across the negative electrostatic latent image which is on the surface of the photoconductive material. As the magnetic brush passes over the areas of the photoconductive material which have residual negative charge thereon, the electrostatic attraction between the charged pigmented resin particles and the oppositely charged image areas in the photo-conductive material is greater than the attraction between these particles and the ferromagnetic powder, so that the pigmented resin is deposited on the surface of the photoconductive material roughly in proportion to the residual charge on the surface of the photoconductive layer. By selecting a resin with a low melting point, the developed image can then be fixed to the surface of the paper by heating to a temperature above the melting point of the resin, but below the charring temperature of the paper. The resin in the pigmented resin compositions can be varied, depending upon the effects desired and the type of copy which is being reproduced. Such resins may be the same as those employed in the insulating layer coated on the paper support, such as styrene-butadiene resin, etc. The particle size of the pigmented resin used in development can vary, although the range of 0.1 to 25 microns is adequate for most purposes. Various pigments can be used in the resin developing compositions. The ability of the pigmented resin to accept a positive charge is dependent upon the type of resin selected. The pigment merely serves to impart color to the resin and probably imparts very little, if any, influence on the overall charge of the pigmented resin.

The following examples will serve to illustrate the manner of using the optically sensitized photoconductive materials of my invention.

EXAMPLE

100 mg. of 3-ethyl-5-[(3)-carboxymethyl-2(3H)-benzoxazolylidene)ethylidene]rhodanine were dissolved in 126 cc. of methanol containing a trace of triethylamine to facilitate dissolving of the dye. There were then added 60 g. of zinc oxide (Florence White Seal No. 7, New Jersey Zinc Company) and the mixture stirred for 30 seconds in a Waring Blendor. The resulting slurry was filtered and the treated zinc oxide filter cake was again placed in the Waring Blendor along with another 126 ml. portion of methanol and stirred for 30 seconds. The slurry was again filtered and the dyed zinc oxide filter cake was broken up and allowed to dry in the air. A mixture of 50 g. of the treated zinc oxide, 18.2 g. of Plaskon ST–856 (Allied Chemical & Dye Corp.) (a silicone-alkyd resin), and 51.8 g. of xylene was placed in a Waring Blendor for 30 minutes. The resulting viscous mixture or dope of zinc oxide was coated on a glossy, single-weight baryta coated paper stock at a coverage of approximately 5 g./ft.^{2}. The coated paper was then charged under a corona discharge and exposed for one-half second in a sensitometer to tungsten illumination. The exposed coating was then developed by the magnetic brush technique described above using small iron particles and black pigmented sulfur. Finally, the image was fixed by fusing the black pigmented sulfur to the paper surface by applying heat. A duplicate coating was treated in the same manner, with the sensitizing dye being omitted, this coating serving as a control.

The electrical characteristics of the control and dye-treated coatings with respect to initial charge and dark decay were essentially the same. However, the speed of the dye-treated coating was approximately twenty times that of the coating containing no sensitizing dye.

As mentioned above, the merocyanine dyes of my invention can be combined with the zinc oxide by simply dipping the coated surface of zinc oxide into a solution of the merocyanine dye. This solution can be an aqueous solution or a solution in an organic solvent, depending upon the solubility characteristics of the particular dye. Methanol, pyridine, benzene, etc. are suitable solvents for many of the dyes of my invention.

In a manner similar to that described above, a number of merocyanine dyes were used to sensitize previously coated zinc oxide by the dip technique. The results of such sensitization are given below, together with the result obtained for a coating which was not treated with any merocyanine dye. The untreated sample is identified as the control.

Table I

Dye No.	Percent Concentration of Dye Solution by Weight	Relative White Light Speed
None (control)		100
2	0.1	3,000
4	0.1	3,000
5	0.1	2,500
6	0.01	2,000
7	0.005	800
8	0.1	3,000

In the manner illustrated above, other carboxyl-sub-

stituted dyes were used to sensitize photoconductive elements comprising a relatively thin layer of photoconductive zinc oxide. The following table (Table II) illustrates the speed increase afforded by using the carboxyl-substituted dyes of my invention. The dyes were incorporated in the photoconductive elements by immersing the photoconductive elements in a solution containing dye in the concentration shown in the table. Where a combination of solvents was used to obtain solution, a small amount of dye (e.g., 2 mg.) was wet with a small amount of the first solvent containing a rather large amount of the second named solvent. The requisite amount of the second solvent was then added to complete solution (or in some cases, the dye was dissolved in a small amount of the first solvent alone and a much larger amount of the second solvent added). The immersed samples were then thoroughly dried and exposed in an intensity scale sensitometer to tungsten illumination and in a spectrograph. The relative white light speeds of the exposed coatings are shown in the table after development of the exposed sample by means of the magnetic brush technique described above.

Where the sensitizing dye has its maximum absorption in the blue region of the spectrum, an exposing source other than tungsten illumination, which has its maximum output in the blue region of the spectrum, is recommended. For example, fluorescent lamps have their maximum output in the blue and ultra-violet regions of the spectrum.

Table II

Dye	Solvent and percent conc.	Relative Speed
Control		100
9	NEt_3+MeOH .01	>1,000
11	MeOH .01	>1,000
12	MeOH .01	>1,000
16	MeOH .01	>1,000
17	MeOH .01	>1,000
18	MeOH .01	>1,000
19	Ocp + Acet .01	>1,000
20	MeOH .01	ca 1,000
22	Acet .01	>1,000
23	Acet .01	>1,000

MeOH=methanol.
NEt_3=triethylamine.
Acet=acetone.
Ocp=o-chlorophenol.

The dyes of our invention can be used in the form containing free carboxyl groups, or as salts (e.g., triethylamine, sodium, pyridine, etc.) of such carboxyl group. The term carboxyl as used herein means either —COOH or a salt of this radical (e.g., alkali metal, organic amine, ammonium).

In a manner similar to that described above, other merocyanine dyes can be used to sensitize photoconductive zinc oxide compositions either by mixing the dye with the zinc oxide prior to coating, or by the immersion technique described above. In some instances, there is a material increase in the range of spectral sensitivity of the photoconductive zinc oxide compositions with a concomitant increase in speed. In order to extend the sensitivity to longer wavelengths, sensitizing dyes containing a polymethine chain of several units can be employed. For example, the sensitivity can be extended to longer wavelengths using such dyes as 3-(p-carboxyphenyl)-5-[(3 - ethyl - 2(3H) - benzoxazolylidene)-2-butenylidene] rhodanine, 3-carboxymethyl-5-[(3-ethyl-2(3H)-benzoxazolylidene)-2-butenylidene]rhodanine, etc.

Merocyanine dyes containing a carboxymethyl or a β-carboxyethyl group attached to one of the nitrogen atoms of the heterocyclic nuclei have been found to be particularly useful in practicing my invention.

As indicated above, the merocyanine dyes useful in practicing my invention can be prepared according to techniques well known to those skilled in the art. Two basic methods of preparation can be used to advantage. One method comprises reacting a cyclammonium quaternary salt containing in a reactive position an acetylated aminovinyl-, butadienyl or hexatrienyl group with a keto-methylene compound containing no substituent in the reactive methylene position. A second method comprises reacting a cyclammonium quaternary salt containing a reactive methyl group in a reactive position with a Dains et al. type intermediate.

Polymethine dyes or "open-chain" merocyanine dyes can advantageously be prepared according to methods well known to those skilled in the art, such as is described in the following references:

U.S. 2,693,472 issued November 2, 1954
Brit. 674,003 issued June 18, 1952
Brit. 681,738 issued October 29, 1952
Brit. 704,770 issued March 3, 1954
Brit. 704,840 issued March 3, 1954
French 1,112,494 issued November 16, 1955

The following examples will serve to illustrate the preparation of two "open-chain" merocyanine dyes which are useful in practicing my invention.

EXAMPLE A

3 - β - carboxyethyl - 2-(3,3-dicyanoallylidene)benzothiazoline (dye 3) was obtained when 3.49 g. of 3-β-carboxyethyl-2-methyl-benzothiazolium iodide, 3.3 g. of malononitrile, 2.9 g. of ethyl orthoformate and 2.02 g. of triethylamine were heated together in 15 ml. of pyridine solution for 10 minutes. After chilling the reaction mixture, the dye was collected on a filter and washed with methyl alcohol. The yield of dye was 32% crude and 20%, in two crops, after two recrystallizations from methyl alcohol. The red crystals lost solvent at about 205° C. and then melted at 216–217° C. with decomposition.

Dye 9 above was prepared by condensing 2-β-acetanilidovinyl-3-ethyl-2(3H)-benzothiazolium iodide with 3-carboxy-5-pyrazolone in the presence of triethylamine.

EXAMPLE B

3 - carboxymethyl-2-(3,3-dicyanoallylidene)benzothiazoline (dye 4) was obtained when 2.88 g. of 3-carboxymethyl-2-methylbenzothiazolium bromide, 3.3 g. of malononitrile, 2.9 g. of ethyl orthoformate, and 2.02 g. of triethylamine were heated together in 15 ml. of pyridine solution for 10 minutes. The cool reaction mixture was stirred with 200 ml. of ether. After chilling the mixture, the dye was collected on a filter. The yield of dye was 34% crude and 13% after two recrystallizations from methyl alcohol. The orange needles melted at 221–222° C. with decomposition.

The accompanying drawing illustrates schematically the increased spectral range of sensitivity provided by three of the dyes useful in practicing my invention. In FIGURES 1, 2 and 3, the solid curves show the range of sensitivity as well as the region of maximum sensitivity. Exposures were made in a spectrograph in the usual manner using tungsten illumination.

In FIGURE 1, the solid curve represents the sensitivity of a photoconductive element comprising a relatively thin layer of photoconductive zinc oxide sensitized with 3-carboxy - 4 - [(3-ethyl-2(3H)-benzothiazolylidene)ethylidene]-5-pyrazolone. The relative speed of this coating corresponds to that of dye 9 in Table II.

In FIGURE 2, the solid curve represents the sensitivity of a photoconductive element comprising a relatively thin layer of photoconductive zinc oxide sensitized with 5-[(5-carboxy-3-methyl-2(3H) - benzoxazolylidene)ethylidene]-2,4-thiazolidinedione. The speed value for this coating corresponds to that of dye 20 in Table II above.

In FIGURE 3, the solid curve represents the sensitivity of a photoconductive element comprising a relatively thin layer of photoconductive zinc oxide sensitized with 3-carboxymethyl - 5 - [(3 - ethoxycarbonylmethyl-2(3H)-thiazolinylidene)isopropylidene]rhodanine. The speed value

for this coating corresponds to that of dye 16 in Table II above.

It has been found that the dyes of my invention containing a free carboxyl group have a markedly improved sensitizing action toward zinc oxide as compared with the corresponding dyes containing no free carboxyl group. This appears to be true regardless of the manner by which the carboxyl group is attached to the molecule of the sensitizing dye. In the compositions of the present invention, the carboxyl-containing dyes are characterized consistently by increased speeds as compared with dyes containing no free carboxyl group. In silver halide photography, the carboxyl and carboxyl-free dyes frequently have about the same sensitizing efficiency. This is illustrated in the following two tables. In these tables, the coatings were prepared by the mixing technique described in above "Example" and the coatings were then dried, exposed, and "developed" by the magnetic brush technique described. The results obtained are summarized below.

Table III

Dye	Conc., mols. dye/56 g. ZnO	Relative Speed
Control	0	100
1	5.6×10^{-5}	420
A	5.6×10^{-5}	91

A=3-ethyl-5-(3-ethyl-2(3H)-benzothiazolylidene)-rhodanine.

Table IV

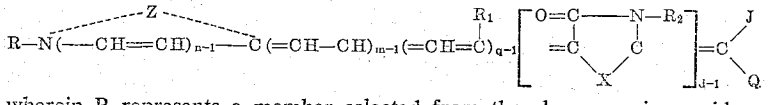
Dye	Conc. (percent by weight)	Relative Speed
Control		100
B	0.1	400
7	0.005	800
C	0.1	200
5	0.1	2,500
6	0.01	2,000

B=3 - ethyl - 5 - [(3 - ethyl - 2(3H) - benzothiazolylidene) - ethylidene] rhodenine.
C=3 - ethyl - 5 - [(3 - ethyl - 2(3H) - benzoxazolylidene) - ethylidene] rhodanine.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What I claim and desire secured by Letters Patent of the United States of America is:

1. A photoconductive composition comprising photoconductive zinc oxide, a high dielectric insulator for said zinc oxide, and a merocyanine dye selected from those represented by the following general formula:



wherein R represents a member selected from the class consisting of an alkyl group, a hydroxyalkyl group, an alkoxyalkyl group, a carboxyalkyl group, a sulfoalkyl group, a carbalkoxyalkyl group, an acyloxyalkyl group, and an aralkyl group, R_1 represents a member selected from the class consisting of a hydrogen atom, an alkyl group and an aryl group, R_2 represents a member selected from the class consisting of a hydrogen atom, an alkyl group, a hydroxyalkyl group, a carbalkoxyalkyl group, and an aryl group, X represents a member selected from the class consisting of an oxygen atom, a sulfur atom and a NR' group wherein R' represents a member selected from the class consisting of an alkyl group and an aryl group, *n*, *q* and *d* each represents a positive integer of from 1 to 2, *m* represents a positive integer of from 1 to 3, Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the class consisting of those of the thiazole series, those of the benzothiazole series, those of the naphthothiazole series, those of the thianaphtheno-7',6',4,5-thiazole series, those of the oxazole series, those of the benzoxazole series, those of the naphthoxazole series, those of the selenazole series, those of the benzoselenazole series, those of the naphthoselenazole series, those of the thiazoline series, those of the 2-quinoline series, those of the 4-quinoline series, those of the 1-isoquinoline series, those of the 3,3-dialkylindolenine series, those of the 2-pyridine series and those of the 4-pyridine series, J represents a member selected from the class consisting of a cyano group and the atoms in combination with Q necessary to complete a heterocyclic ring selected from the class consisting of those of the pyrazolone series, those of the isoxazolone series, those of the oxindole series, those of the 2,4,6-triketohexahydropyrimidine series, those of the 2-thio-4,6-diketohexahydropyrimidine series, those of the rhodanine series, those of the 2(3H)-imidazo[1,2-a]pyridone series, those of the 5,7 - dioxo-6,7-dihydro-5-thiazolo[3,2-a]pyrimidine series, those of the 2-thio-2,4-oxazolidinedione series, those of the thianaphthenone series, those of the 2-thio-2,5-thiazolidinedione series, those of the 2,4-thiazolidinedione series, those of the thiazolidinone series, those of the 4-thiazolinone series, those of the 2-imino-2,4-oxazolinone series, those of the 2,4-imidazolinedione series, those of the 2-thio-2,4-imidazolinedione series, and those of the 5-imidazolinone series, Q, when J represents a cyano group, represents a member selected from the class consisting of a cyano group and a carbalkoxyl group, provided *d* represents one when J represents a cyano group and Q represents a member selected from the class consisting of a cyano group and a carbalkoxyl group, and provided further that said merocyanine dye contains at least one carboxyl group attached to a carbon atom thereof.

2. A photoconductive composition comprising photoconductive zinc oxide, a high dielectric insulator for said zinc oxide and, 3-β-carboxyethyl - 2 - (3,3 - dicyanoallylidene)benzothiazoline.

3. A photoconductive composition comprising photoconductive zinc oxide, a high dielectric insulator for said zinc oxide and, 3-carboxymethyl - 5 - [(3-methyl-2(3H)-thiazolinylidene)isopropylidene]rhodanine.

4. A photoconductive composition comprising photoconductive zinc oxide, a high dielectric insulator for said zinc oxide and, 3-ethyl - 5 - [(3 - carboxymethyl-2(3H)-benzoxazolylidene)ethylidene]rhodanine.

5. A photoconductive composition comprising photoconductive zinc oxide, a high dielectric insulator for said zinc oxide and, 3-carboxy-4-[(3 - ethyl - 2(3H) - benzothiazolylidene)ethylidene]-5-pyrazolone.

6. A photoconductive composition comprising photoconductive zinc oxide, a high dielectric insulator for said zinc oxide and, 4-[3-carboxyethyl-2(3H)-benzoxazolylidene)butenylidene]-3-phenyl-2-isoxazolin-5-one.

7. A photoconductive composition of claim 1 containing a merocyanine dye represented by the structural formula in which *n* represents the integer 1, *m* represents the integer 1, Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series, and when Q and J are combined, they form a heterocyclic nucleus of the rhodanine series.

8. A photoconductive composition of claim 1 containing a merocyanine dye represented by the structural formula in which *n* represents the integer 1, *m* represents the integer 1, Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the thiazoline series,

and when Q and J are combined, they form a heterocyclic nucleus of the rhodanine series.

9. A photoconductive composition of claim 1 containing a merocyanine dye represented by the structural formula in which *n* represents the integer 1, *m* represents the integer 1, Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzoxazole series, and when Q and J are combined, they form a heterocyclic nucleus of the rhodanine series.

10. A photoconductive composition of claim 1 containing a merocyanine dye represented by the structural formula in which *n* represents the integer 1, *m* represents the integer 1, Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzothiazole series, and when Q and J are combined, they form a heterocyclic nucleus of the pyrazolone series.

11. A photoconductive composition of claim 1 containing a merocyanine dye represented by the structural formula in which *n* represents the integer 1, *m* represents the integer 1, Z represents the non-metallic atoms necessary to complete a heterocyclic nucleus of the benzoxazole series, and when Q and J are combined, they form a heterocyclic nucleus of the isoxazolone series.

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