

1

3,132,942

ACID-SUBSTITUTED DYES FOR ELECTROPHOTOGRAPHIC ZINC OXIDE COMPOSITIONS

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6 Claims. (Cl. 96—1)

This invention relates to spectrally 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. 645,419, filed March 12, 1957, 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

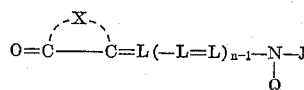
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strongly dyeing the zinc oxide layer more than offsets the sensitivity which is supplied to the feebly sensitive zinc oxide. That is, it is generally desirable to have some means of sensitizing the zinc oxide which does not permanently color the zinc 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 spectrally sensitizing zinc oxide photoconductive layers in a useful manner. Another object is to provide a means of spectrally sensitizing zinc oxide photoconductive layers by means of acid-substituted hemioxonol or oxonol dyes. Other objects will become apparent from a consideration of the following description and examples.

The acid-substituted hemioxonol dyes which I have found to be particularly useful in practicing my invention comprise those dyes represented by the following general formula:

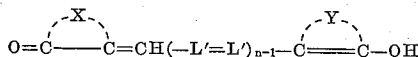
(I)



wherein L represents a methine group (i.e., unsubstituted or substituted by alkyl groups, such as methyl, ethyl, etc., or wherein an alkylene group, such as ethylene, neopentylene, etc., is attached to two methine groups thus completing a carbocyclic ring), n represents a positive integer of from 1 to 3, J represents a hydrogen atom, an alkyl group, such as methyl, ethyl, n-propyl, n-butyl, etc. (e.g., an alkyl group containing from 1 to 4 carbon atoms), or an acyl group, such as acetyl, propionyl, benzoyl, etc. (e.g., a carboxylic acyl group containing from 2 to 7 carbon atoms), Q represents an alkyl group, such as methyl, ethyl, n-propyl, n-butyl, etc. (e.g., an alkyl group containing from 1 to 4 carbon atoms) or an aryl group, such as phenyl, chlorophenyl, tolyl, diphenyl, naphthyl, etc. (especially a monocyclic aryl group of the benzene series), or J and Q together represent the non-metallic atoms necessary to complete a heterocyclic nucleus, such as piperidyl, morpholinyl, tetrahydroquinolyl, piperazyl, etc., and X represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring, provided said dye contains at least one acid radical, such as carboxyl or sulfo (including water-soluble alkali metal, ammonium, etc., salts thereof), attached to a carbon atom thereof.

The acid-substituted oxonol dyes which I have found to be particularly useful in practicing my invention comprise those dyes represented by the following general formula:

(II)



wherein n has the values given above, L' represents a methine group, such as those represented by L above (e.g., $-\text{CR}'=$, wherein R' represents a hydrogen atom or an alkyl group, such as methyl, ethyl, etc.), and X and Y each represents the non-metallic atoms necessary to complete a heterocyclic nucleus containing from 5 to 6 atoms in the heterocyclic ring. It is to be understood that by the term oxonol dye, I intend to include not only oxonol dyes as such, but the salts of such dyes, such as alkali metal salts (e.g., sodium, potassium, etc.), ammonium, and organic amine salts, such as triethylamine, pyridine, aniline, N,N-dimethylaniline, etc., provided said dye contains at least one acid radical, such as carboxyl or sulfo

(including water-soluble alkali metal, ammonium, etc., salts thereof), attached to a carbon atom thereof.

Typical heterocyclic nuclei as defined by X and Y above include, for example, such nuclei as a thiazolone nucleus, for example, a 2,4(3,5)-thiazolodione nucleus, such as 2,4(3,5)-thiazolodione, 3-alkyl-2,4(3,5)-thiazolodiones (e.g., 3-ethyl-2,4(3,5)-thiazolodione), 3-phenyl-2,4(3,5)-thiazolodione, 3- α -naphthyl-2,4(3,5)-thiazolodione, a 2-thio-2,4(3,5)-thiazolodione (a rhodanine) nucleus, such as a 3-alkyl-2-thio-2,4(3,5)-thiazolodione (3-alkylrhodanine) (e.g., 3-ethyl-2-thio-2,4(3,5)-thiazolodione or 3-ethylrhodanine), 3-phenyl-2-thio-2,4(3,5)-thiazolodione (3-phenylrhodanine) or 3- α -naphthyl-2-thio-2,4(3,5)-thiazolodione (3- α -naphthylrhodanine) nuclei or 3-(1-benzothiazyl) - 2 - thio-2,4(3,5) - thiazolodione (3-(1-benzothiazyl) rhodanine) nuclei, a 2-alkylmercapto-4(5)-thiazolone nucleus, such as 2-ethylmercapto-4(5)-thiazolone, a thiazolidone nucleus, such as 4-thiazolidone or its 3-alkyl (e.g., ethyl), 3-phenyl or 3- α -naphthyl derivatives, a 2-alkylphenylamino-4(5)-thiazolone nucleus or a 2-diphenylamino-4(5)-thiazolone nucleus; an oxazolone nucleus, for example, a 2-thio-2,4(3,5)-oxazolodione nucleus, such as a 3-alkyl-2-thio-2,4(3,5)-oxazolodione nucleus (e.g., 3-ethyl-2-thio-2,4(3,5)-oxazolodione) and a 2-imino-2,4(3,5)-oxazolone (a pseudohydantoin nucleus; a 2-alkylmercapto-5(4)-imidazolone nucleus, such as 2-n-propylmercapto-5(4)-imidazolone; a thianaphthenone nucleus, such as 2(1)-thianaphthenone or 1(2)-thianaphthenone, a pyrazolone nucleus; an oxindole nucleus, such as 2,4-dihydro-3-ketoinole, and like five-membered heterocyclic nuclei; a 2,4,6-triketohexahydropyrimidine nucleus, for example, barbituric acid or 2-thiobarbituric acid as well as their 1-alkyl (e.g., 1-ethyl) or 1,3-dialkyl (e.g., 1,3-diethyl) derivatives; a 3,4-dihydro-2(1)-quinolone nucleus, such as 3,4-dihydro-2(1)-quinolone (dihydrocarbo-styryl); a 3,4-dihydro-2(1)-quinoxalone nucleus, such as 3,4-dihydro-2(1)-quinoxalone (oxydihydroquinoxaline); 3-phenomorpholone (1,4,3 - benzoxazine - 3(4) - one or benzo- β -morpholone) nuclei; 1,4,2 - benzothiazine-3(4)-one (ketodihydrobenzoparathiazine) nuclei, and the like six-membered heterocyclic nuclei.

Hemioxonol dyes which are useful in practicing my invention include the following:

- (1) 5-(5-anilino-2,4-pentadienylidene)-3-carboxymethylrhodanine.
- (2) 1-(4-diethylamino - 2 - sulfobenzylidene)-2(1)-thionaphthenone.
- (3) 5-(4-dimethylamino - 2 - sulfobenzylidene)barbituric acid.
- (4) 1-(2-sulfobenzylidene) - 2(1) - thionaphthenone sodium salt.
- (5) 1-(3-carboxyphenyl)-4 - (4 - dimethylaminobenzylidene)-3-methylpyrazolin-5-one.
- (6) 4-(3-chloro - 4 - diethylaminobenzylidene)-3-methyl-1-(3-sulfophenyl)pyrazolin-5-one.
- (7) 2 - mercapto-5-(4-diethylamino-2-sulfobenzylidene)-4(5)-thiazolidone.

The methods of preparing the above hemioxonol dyes have been previously described in the prior art. Among the patents describing the preparation of such dyes are the following:

U.S. 2,089,729, issued on August 10, 1937
 U.S. 2,165,339, issued on July 11, 1939
 U.S. 2,186,608, issued on January 9, 1940
 U.S. 2,216,441, issued on October 1, 1940
 Br. 431,652, issued on July 12, 1935
 Br. 396,646, issued on August 10, 1933
 Fr. 1,038,333, issued on May 6, 1953

Oxonol dyes which are useful in practicing my invention include the following:

- (8) Bis[3-methyl - 1 - p-sulfophenyl-5-pyrazolone-(4)]-pentamethineoxonol.

- (9) [3 - carboxymethyl-1-phenyl-5-pyrazolone-(4)]-[1,3-di-p-phenetyl barbituric acid-(5)]pentamethineoxonol.
- (10) [1-p-carboxyphenyl - 3 - methyl-5-pyrazolone-(4)]-[3-methyl-1-phenyl - 5 - pyrazolone-(4)]pentamethineoxonol.
- (11) [1-p-carboxyphenyl - 3 - pentadecyl]-5-pyrazolone-(4)]-[3-methyl-1-phenyl - 5 - pyrazolone - (4)]pentamethineoxonol.
- (12) [1 - p-carboxyphenyl-3-methyl-5-pyrazolone(4)]-[3-methyl-1-phenyl-5-pyrazolone(4)]pentamethineoxonol.
- (13) Bis[3-carboxy - 1 - phenyl - 5 - pyrazolone(4)]trimethineoxonol.
- (14) Bis[3 - methyl-1-p-sulfophenyl-5-pyrazolone(4)]trimethineoxonol.
- (15) [1 - p-carboxyphenyl-3-n-pentadecyl-5-pyrazolone-(4)]-[2-cyanoacetylbenzofuran]pentamethineoxonol.

The methods for making the above oxonol dyes have been previously described in the prior art. Among the patents describing the preparation of such dyes are the following:

U.S. 2,241,238, issued on May 6, 1941
 U.S. 2,345,193, issued on March 28, 1944
 U.S. 2,611,696, issued on September 23, 1952
 Br. 418,561, issued on October 19, 1934
 Br. 624,462, issued on June 9, 1949
 Br. 628,837, issued on September 6, 1949
 Br. 663,042, issued on December 12, 1951

The above spectral sensitizing dyes can be combined with the zinc oxide photoconductive material in any convenient manner. For example, the spectral 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 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 sensitizing 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 sensitizing 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 or S-5D, 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.

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 causes a loss or reduction of the negative charge in those portions of the photoconductive 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 photoconductive 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 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 resins, 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 will serve to illustrate the manner of using the spectrally sensitized photoconductive materials of my invention.

A number of dyes represented by the above numbers were dissolved in a suitable solvent, such as water, pyridine, methanol, etc., depending upon the solubility characteristics of the particular dye, and separate sheets of paper coated with unsensitized zinc oxide compositions immersed in the solutions containing the sensitizing dyes. The sensitized zinc oxide papers were then dried in air in a vertical position. After drying, the strips were charged under a corona discharge and exposed for one-half second in a sensitometer. The exposed coatings were then developed by the magnetic brush technique described above using small iron particles and black pigmented sulfur. Finally, the images were fixed by fusing the black pigmented sulfur to the paper surface by applying heat. A duplicate strip treated in the same manner, with the sensitizing dye being omitted, served as a control. In the following table are listed the results obtained using the spectral sensitizing dyes as identified above.

Dye No.	Percent Concentration of dye solution by weight	Relative white light speed
Control.....		100
1.....	0.05	2,000
8.....	0.05	200
9.....	0.05	2,000
11.....	0.05	1,000
12.....	0.05	3,000
13.....	0.01	800
15.....	0.01	1,000

The dyes of my invention are particularly outstanding in that they are adapted to both immersion sensitization and sensitization by incorporation in the photoconductive compositions prior to coating. Some of the better known dyes, such as Rose Bengal and crystal violet are quite useful in increasing the sensitivity of the zinc oxide in the visible region of the spectrum. However, they have marked staining properties, particularly when the immersion technique of sensitization is employed. The reflectance of zinc oxide coatings dyed with crystal violet is lowered to about 63% in the red region of the spectrum. On the other hand, the dyes of my invention, such as Dye 12, produce coatings having a reflectance of at least about 85% minimum in the visible region of the spectrum.

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 as my invention and desire secured by Letters Patent of the United States is:

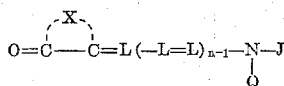
1. A photoconductive composition comprising zinc oxide, a high dielectric, organic, hydrophobic insulator for said zinc oxide, and a sensitizing dye selected from the group consisting of hemioxonol dyes and oxonol dyes, each of said dyes having attached to a carbon atom thereof an acid radical selected from the class consisting of carboxyl and sulfo.

2. A photoconductive composition comprising zinc oxide, a high dielectric insulator for said zinc oxide, and 5-(5'-anilino-2,4-pentadienylydene)-3-carboxymethylrhodaniline.

3. A photoconductive composition comprising zinc oxide, a high dielectric insulator for said zinc oxide, and bis-[3-methyl-1-p-sulphophenyl-5-pyrazolone-(4)]pentamethineoxonol.

4. A photoconductive composition comprising zinc oxide, a high dielectric insulator for said zinc oxide and [1 - p - carboxyphenyl - 3 - methyl - 5-pyrazolone(4)] [3-methyl-1-phenyl-5-pyrazolone(4)] pentamethineoxonol.

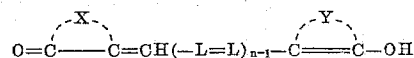
5. An electrophotographic element comprising a support and a relatively thin layer comprising photoconductive zinc oxide, a high dielectric insulator-binder for said zinc oxide and a sensitizing dye selected from those represented by the following general formula:



wherein L represents a methine group, n represents a positive integer of from 1 to 3, J represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms, a carboxylic acyl group containing from 2 to 7 carbon atoms, and radicals which together with and bonded to Q represent the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of piperidyl, morpholinyl, tetrahydroquinolyl and piperazyl, Q, when J represents a member selected from the group consisting of a hydrogen atom, an alkyl group containing from 1 to 4 carbon atoms and a carboxylic acyl group containing from 2 to 7 carbon atoms, represents an alkyl group containing from 1 to 4 carbon atoms and a monocyclic aryl group of the benzene series, and X represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of a thiazolone nucleus, an oxazolone nucleus, a 2-alkylmercapto-5(4)-imidazolone nucleus, a thianaphthenone nucleus, a pyrazolone nucleus, an oxindole nucleus, a 2,4,6-triketohexa-

hydropyrimidine nucleus, a 3,4-dihydro-2(1)-quinolone nucleus, a 3,4-dihydro-2(1)-quinoxalone nucleus, a 3-phenomorpholone nucleus and a 1,4,2-benzthiazine-3(4)-one nucleus, the nitrogen atoms in the heterocyclic rings defined by X being tertiary nitrogen atoms, said hemioxonol dye having attached to a carbon atom thereof an acid radical selected from the class consisting of carboxyl and sulfo.

6. An electrophotographic element comprising a support and a relatively thin layer comprising photoconductive zinc oxide, a high dielectric insulator-binder for said zinc oxide and a sensitizing dye selected from those represented by the following general formula:



wherein L represents a methine group, n represents a positive integer of from 1 to 3, and X and Y each represents the non-metallic atoms necessary to complete a heterocyclic nucleus selected from the group consisting of a thiazolone nucleus, an oxazolone nucleus, a 2-alkylmercapto-5(4)-imidazolone nucleus, a thianaphthenone nucleus, a pyrazolone nucleus, an oxindole nucleus, a 2,4,6-triketohexahydropyrimidine nucleus, a 3,4-dihydro-2(1)-quinolone nucleus, a 3,4-dihydro-2(1)-quinoxalone nucleus, a 3-phenomorpholone nucleus and a 1,4,2-benzthiazine-3(4)-one nucleus, the nitrogen atoms in the heterocyclic rings defined by each of X and Y being tertiary nitrogen atoms, said oxonol dye having attached to a carbon atom thereof an acid radical selected from the class consisting of carboxyl and sulfo.

No references cited.