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USE OF AMINES IN PHOTOCONDUCTOGRAPHIC COATINGS

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This invention concerns the use of amines and photoconductive coatings containing zinc oxide in a resinous binder.

Photoconductography is described in detail in British Patent 188,030, Von Bronk, and British Patent 464,112, Goldman. British Patent 789,309, Berchtold, describes an improvement in the process using a protective layer against photoconductive and recording layers and Belgian Patent 561,403, Johnson et al., describes in considerable detail systems using zinc oxide as a photoconductor.

Photoconductography forms a complete image at one time or at least a non-uniform part of an image as distinguished from facsimile which at any one moment produces only a uniform dot. The present invention is applicable to all forms of photoconductography and cross reference is made to the following series of applications filed July 28, 1960, illustrating various types of photoconductography in which this invention can be applied:

Serial No. 45,940, John W. Castle, Jr., "Photoconductography Employing Reducing Agents."

Serial No. 45,941, Raymond F. Reithel, "Photoconductolithography Employing Nickel Salts," now abandoned.

Serial No. 45,942, Raymond F. Reithel, "Photoconductolithography Employing Magnesium Salts," now U.S. Patent No. 3,053,179.

Serial No. 45,943, Raymond F. Reithel, "Photoconductography Employing Spongy Hydroxide Images," now abandoned.

Serial No. 45,944, Raymond F. Reithel, "Method for Making Transfer Prints Using a Photoconductographic Process."

Serial No. 45,945, Raymond F. Reithel, "Photoconductography Employing Manganese Compounds," now abandoned.

Serial No. 45,946, Raymond F. Reithel, "Photoconductography Employing Molybdenum or Ferrous Oxide," now abandoned.

Serial No. 45,947, Raymond F. Reithel, "Photoconductography Employing Cobaltous or Nickelous Hydroxide," now abandoned.

Serial No. 45,948, Donald R. Eastman, "Electrophotolithography."

Serial No. 45,949, Donald R. Eastman, "Photoconductolithography Employing Hydrophobic Images," now U.S. Patent No. 3,152,969.

Serial No. 45,950, Donald R. Eastman and Raymond F. Reithel, "Photoconductography Employing Electrolytic Images To Harden or Soften Films," now U.S. Patent No. 3,106,516.

Serial No. 45,951, Donald R. Eastman and Raymond F. Reithel, "Photoconductography Employing Absorbed Metal Ions," now abandoned.

Serial No. 45,952, Donald R. Eastman and Raymond F. Reithel, "Photoconductography Employing Spongy Images Containing Gelatin Hardeners," now U.S. Patent No. 3,106,517.

Serial No. 45,953, John J. Sagura, "Photoconductography Employing Alkaline Dye Formation," now U.S. Patent 3,057,787.

Serial No. 45,954, John J. Sagura and James A. Van Allan, "Photoconductography Employing Quaternary Salts," now U.S. Patent No. 3,178,362.

Serial No. 45,955, Franz Urbach and Nelson R. Nail, "Uniform Photoconductographic Recording on Flexible Sheets," now abandoned.

Serial No. 45,956, Franz Urbach and Nelson R. Nail, "High Contrast Photoconductographic Recording," now abandoned.

Serial No. 45,957, Nicholas L. Weeks, "Photoconductography Involving Transfer of Gelatin," now abandoned.

Serial No. 45,958, Donald R. Eastman, "Photoconductolithography Employing Rubeanates," now U.S. Patent No. 3,095,808.

Serial No. 45,959, Donald R. Eastman and Raymond F. Reithel, "Electrolytic Recording with Organic Polymers," now U.S. Patent No. 3,106,155.

Serial No. 46,034, Franz Urbach and Donald Pearlman, "Electrolytic Recording," now abandoned.

In carrying out photoconductographic processes, a coating of zinc oxide in a suitable resinous binder is applied on a conductive substrate such as aluminum foil. Any metal support of high conductivity can be used as the conductive substrate. Another useful substrate is NESA glass. The coating is then moistened using an electrolyte, herein referred to as the developer, which may be a manganese nitrate-silver nitrate solution as described in application Serial No. 45,945 above. It has been desirable to increase the speed, gamma, and D'_{max}, and we have found that increases in these values have been obtained by incorporating amines in the resinous photoconductographic coatings containing zinc oxide. The coatings produced have improved image quality, higher image densities at lower exposures at line copy reproduction, and improved tone quality and definition in continuous-tone reproduction.

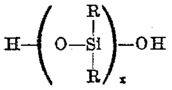
One object of this invention is to increase the speed, gamma, and D'_{max} in zinc oxide resinous photoconductographic coatings. Another object is to produce improved image quality, higher image densities at lower exposures at line copy reproduction, and improved tone quality and definition in continuous-tone reproduction. A further object is to provide a method for improving the quality of photoconductographic coatings by incorporating amines in the resinous binders used in such coatings. An additional object is to provide an improved photoconductographic recording material.

The above objects are obtained by incorporating 0.01 to 4.0% by weight of an ammonium or amine compound in the zinc oxide resinous coating based on the zinc oxide content. The ammonium or amine compounds useful in our invention are those found in two groups. The first group can be defined as NR_3 where the R's may be the same or different and include R being: hydrogen, $(CH_2)_nNH_2$, $n=2$ to 22, $(CH_2CH_2NH)_nH$, $n=1$ to 11, and 1 to 22 carbon alkyl groups derived from fatty acids, i.e., saturated and unsaturated straight chain groups.

The second group is $R_4N^+X^-$ where the R's may be the same or different and include R being 1 to 22 carbon alkyl groups derived from fatty acids, i.e., saturated and unsaturated straight chain groups, and X is a halogen such as chlorine or bromine.

Various resinous binders may be used as carriers for the zinc oxide but we prefer to use a mixture of a styrene-butadiene copolymer, a silicone polymer, and a hydrocarbon polymer derived from the deep cracking of petroleum. The styrene-butadiene resin may be one of those well known in the art; see Zwicker, Ind. Eng. Chem., 44, 774–786, especially pages 778–779, and Bovey et al., Emulsion Polymerization, interscience Publishers, Inc., N.Y., 1955, pages 406–7. The butadiene-styrene resins useful in our invention are those in which butadiene and styrene are polymerized in a ratio of butadiene to styrene of 60:40 to 20:80, although the preferred ratio is from 45:55 to 30:70.

The silicone may be an organo polysiloxane resin having the following general formula:



$$H\left(O-\overset{R}{\underset{R}{Si}}\right)_x-OH$$

where x is an integer from 6 to 40, and R is a methyl or phenyl radical, so chosen that both radicals on any given silicon atom are identical and the molar ratio of methyl to phenyl radicals varies from 4:1 to 1:4. Higher molecular weight polysiloxanes are operable for use in this invention as long as they are sufficiently compatible with the styrene-butadiene resin to permit coating.

The silicone resins may be obtained by the catalytic equilibration procedure disclosed in chapter 6 of E. G. Rochow's "Introduction to the Chemistry of the Silicones," John Wiley & Sons, Inc., New York, second edition, 1951. Mixtures of dichlorodiphenylsilane and dichlorodimethylsilane are treated with the appropriate quantity of water to hydrolyze the above chlorosilanes with concurrent polymerization. For our purpose, the mixture composition may vary from a ratio of 20 molar percent of dichlorodiphenylsilane and 80 molar percent of dimethyldichlorosilane to a ratio of 80 molar percent dichlorodiphenylsilane and 20 molar percent dichlorodimethylsilane although the preferred mixture is 1:1 on a molar basis.

The hydrocarbon polymer derived from the deep cracking of petroleum is a pure hydrocarbon thermoplastic terpene polymer composed essentially of β-pinene.

Other resinous binders useful as carriers for the zinc oxide are polystyrene, chlorinated rubber, rubber chlorohydrate, shellac, cellulose ethers, cellulose esters, poly(vinyl butyral), poly(vinyl chloride), poly(vinyl acetate) and copolymers of vinyl chloride and vinyl acetate.

Inert solvents may be used to form a coating mixture and may be selected from mixtures of various solvents such as toluene, 2-butanone, 2-methyl-4-pentanone, methanol, ethanol, xylene, benzene, dioxane, acetone, Solvesso 100, 50:50 xylene-hexane, and the like, which are common solvents for at least one of the components of the resinous mixture.

After being coated on the substrate and dried, the photoconducting layer should have a weight in the range of 2 to 8 g./ft.^{2}, with the preferred weight being about 4 g./ft.^{2}.

The zinc oxide which can be used in our invention is known as photoconductive zinc oxide. It may be prepared by the French process, the American process, or any other process which produces photoconductive zinc oxide. It may be modified and/or sensitized in accordance with known methods or in accordance with the teaching of U.S. patent application Ser. No. 75,753 in the names of Blake and Natale, entitled "Surface Modification of Zinc Oxide," now abandoned. Other binders may be used including those described in U.S. patent application Serial No. 73,184 in the names of Stahly and Herr, entitled "Superior Binders for Photoconductive Layers Containing Zinc Oxide," now U.S. Patent No. 3,132,941. The following examples are intended to illustrate our invention but are not intended to limit it in any way.

EXAMPLE 1

Material	Solids, grams	Total, grams
Butadiene-styrene Copolymer (30% solution in toluene)	64	213.4
Polysiloxane Silicone Resin (60% solution in toluene)	8	13.3
Hydrocarbon Thermoplastic Terpene Polymer (60% solution in toluene)	8	13.3
ZnO	240	240.0
Toluene		302.0
Methanol		19.2
Sodium Dioctyl Sulfosuccinate		0.17
N-alkyltrimethylenediamine		0.5

NOTE.—Alkyl represents a mixture of hexadecyl, octadecenyl, octadecadienyl, and octadecatrienyl in approximately 1:1:2.5:5 by weight.

Toluene, methanol, sodium dioctyl sulfosuccinate, N-alkyltrimethylenediamine, and zinc oxide are placed in a Waring Blendor and mixed for 20 minutes. The butadiene-styrene copolymer, polysiloxane silicone resin, and hydrocarbon thermoplastic terpene polymer are added and mixed an additional 5 minutes. This composition is then coated on an aluminum laminated support.

A sheet of this coating containing the photoconductive layer prepared from the composition described above is exposed for 15 seconds to 600 f.c. tungsten radiation incident upon a 0–3, 0.3 log E increment silver step tablet in contact with the photoconductive surface. Upon termination of exposure the layer is developed in a manganese nitrate-silver nitrate developer-toner system by using a viscous sponge brush electrode, held at 80 volts positive with respect to the zinc oxide layer, with a 1% manganous nitrate solution and 10 strokes development. A faint yellowish-brown image of manganous hydroxide is produced on the surface of the photoconductor. This image is converted to the black adsorption complex of manganese dioxide and reduced silver chemically by treating it with 5% silver nitrate solution. The H and D curve prepared from this sample indicated that 1,860 f.c.s.[1] exposure was necessary to produce a density of 0.4 above base.

A sample prepared identically from this same composition of materials but with the N-alkyltrimenthylenediamine omitted was exposed and developed in the same manner. The H and D curve prepared from this sample indicated that 7,420 f.c.s.[1] exposure was necessary to produce a density of 0.4 above base.

From these data, it is obvious that a coating containing N-alkyltrimethylenediamine requires approxiamtely one-fourth the exposure required by a coating containing no N-alkyltrimethylenediamine to produce the same density. Therefore, the incorporation of N-alkyltrimethylenediamine to zinc oxide dispersions increases photographic speed by four times.

EXAMPLE 2

Optically sensitized zinc oxide dispersions:

Material	Solids, grams	Total, grams
Butadiene-styrene Copolymer (30% solution in toluene)	64	213.4
Polysiloxane Silicone Resin (60% solution in toluene)	8	13.3
Hydrocarbon Thermoplastic Terpene Polymer (60% solution in toluene)	8	13.3
ZnO	240	240.0
Toluene		302.0
Methanol		19.2
N-alkyltrimethylenediamine		0.5
Sens. dye (Total), mg		86.4

Toluene, N-alkyltrimethylenediamine, and zinc oxide are placed in a Waring Blendor and mixed 20 minutes. Sensitizing dye (Rose Bengal) dissolved in methanol is

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[1] Foot-candle seconds.

added and the mixture is mixed an additional 5 minutes. Butadiene-styrene copolymer, polysiloxane silicone resin, and hydrocarbon thermoplastic terpene polymer are added and the mixture is mixed 5 minutes. This composition is then coated on an aluminum laminated support.

A sheet of this coating containing the photoconductive layer prepared from the composition above was exposed for 5 seconds to 400 f.c. tungsten radiation as described in Example 1. Upon termination of exposure, the coating was developed as in Example 1. The H and D curve prepared from this sample indicated that 28 f.c.s. exposure was necessary to produce a density of 0.6 above base.

A sample prepared identically from this same composition of materials but with the N-alkyltrimethylenediamine omitted was exposed and developed in the same manner. The H and D curve prepared from this sample indicated that 250 f.c.s. exposure was necessary to produce a density of 0.6 above base.

From these data, it is obvious that the N-alkyltrimethylenediamine reduces the exposure required to produce the same density to approximately one-ninth that required by a coating containing no N-alkyltrimethylenediamine. Therefore, the incorporation of N-alkyltrimethylenediamine to optically sensitized zinc oxide dispersions increases photographic speed by nine times.

EXAMPLE 3

Chemically (HCl gas) sensitized zinc oxide dispersion:

Material	Solids, grams	Total, grams
Butadiene-styrene Copolymer (30% solution in toluene)	80.8	270
Polysiloxane Silicone Resin (60% solution in toluene)	10.1	17
Hydrocarbon Thermoplastic Terpene Polymer (60% solution in toluene)	10.1	17
ZnO	403.0	403
Toluene		450
Methanol		42
HCl (gas) atmos. press., cc		451
Sodium Dioctyl Sulfosuccinate		0.17
N-alkyltrimethylenediamine		0.5
Polysiloxane Silicone Resin (60% solution in toluene)		0.1
Sens. Dye (Total), mg		8.25

Toluene, polysiloxane silicone resin, N-alkyltrimethylenediamine, sodium dioctyl sulfosuccinate, and zinc oxide are placed in a Waring Blendor and mixed 20 minutes. HCl gas is added slowly during rapid agitation and the mixture is mixed an additional 30 minutes. Sensitizing dye (Crystal Violet) dissolved in methanol is added and the mixture is mixed an additional 5 minutes. Butadiene-styrene copolymer, polysiloxane silicone resin, and hydrocarbon thermoplastic terpene polymer are added and the mixture is mixed an additional 5 minutes. This composition is then coated on an aluminum laminated support.

A sheet of this coating containing the photoconductive layer prepared from the composition above was exposed for 5 seconds to 400 f.c. tungsten radiation as described in Example 1. Upon termination of exposure, the coating was developed as in Example 1. The H and D curve prepared from this sample indicated that 53 f.c.s. exposure was necessary to produce a density of 0.6 above base.

A sample prepared identically from this same composition of materials but with the N-alkyltrimethylenediamine omitted was exposed and developed in the same manner. The H and D curve prepared from this sample indicated that 234 f.c.s. exposure was necessary to produce a density of 0.6 above base.

From these data, it is obvious that the N-alkyltrimethylenediamine reduces the exposure required to produce the same density to approximately one-fourth that required by a coating containing no N-alkyltrimethylenediamine. Therefore, the incorporation of N-alkyltrimethylenediamine to chemically sensitized oxide dispersions increases speed by four times.

EXAMPLE 4

When N-alkyltrimethylenediamine in Example 2 is replaced by the amine or quaternary ammonium salts listed in Table I below, a photographic speed increase results. These speed increases, corresponding to those obtained with N-alkyltrimethylenediamine, are summarized in Table I.

Table I

Amine or ammonium compound:	Photographic speed increase
Ammonia	+4×
n-Butylamine	+8×
n-Hexylamine	+8×
2-ethylhexylamine	+8×
n-Heptylamine	+12×
n-Tetradecylamine	+6×
n-Docosylamine	+8×
Di-n-butylamine	+6×
Tri-n-butylamine	+6×
Dodecamethylenediamine	+8×
n-Dodecyldiethylenetriamine	+10×
Trimethylalkylammonium chloride[1]	+8×
Dimethyldialkylammonium chloride[1]	+6×

[1] Alkyl here represents a mixture of octadecenyl, octadecyl, eicosyl and docosyl in approximately 1 : 3 : 3 : 3 by weight.

EXAMPLE 5

Optically sensitized zinc oxide dispersion:

Material	Solids, grams	Total, grams
Butadiene-styrene Copolymer (30% solution in toluene)	64	213.4
Polysiloxane Silicone Resin (60% solution in toluene)	8	13.3
Hydrocarbon Thermoplastic Terpene Polymer (60% solution in toluene)	8	13.3
ZnO	400	400.0
Toluene		302.0
Methanol		19.2
N-alkyltrimethylenediamine		0.5
Sodium Bistridecyl Sulfosuccinate		0.17
Sens. dye (Total), mg		86.4

Toluene, N-alkyltrimethylenediamine, sodium bistridecyl sulfosuccinate, and zinc oxide are placed in a Waring Blendor and mixed 20 minutes. Sensitizing dye (Rose Bengal) dissolved in methanol is added and the mixture is mixed an additional 5 minutes. Butadiene-styrene copolymer, polysiloxane silicone resin, and hydrocarbon thermoplastic terpene polymer are added and the mixture is mixed 5 minutes. This composition is then coated on an aluminum laminated support.

A sheet of this coating containing the photoconductive layer prepared from the composition above was exposed for 5 seconds to 400 f.c. tungsten radiation as described in Example 1. Upon termination of exposure the coating was developed using an electrolytic developing system involving a developing solution of the following composition:

A solution of 8.5 grams of silver nitrate in 250 ml. distilled water was slowly added with stirring to a solution of 8.0 grams of the mercaptoethylated 2-aminoethanol, $HOCH_2CH_2NH(CH_2CH_2S)_nH$, where n equals 1.67 average, in 250 ml, distilled water, and the mixture filtered through filter paper.

This solution was applied using a viscous sponge electrode held at 60 volts positive to the zinc oxide layer. A neutral silver image was produced in the exposed areas on the surface of the photoconductor. The H and D curve prepared from this sample indicated that 950 f.c.s. exposure was necessary to produce a density of 0.6 above base.

An optically sensitized zinc oxide coating was prepared identically using the same composition of materials except that the N-alkyltrimethylenediamine was omitted. This coating was exposed and developed in the same manner. The H and D curve prepared from this sample indicated that 9000 f.c.s. exposure was necessary to produce a density of 0.6 above base.

From these data, it is obvious that the N-alkyltrimethylenediamine reduces the exposure required to produce the same density to approximately one-tenth that required by a coating containing no N-alkyltrimethylenediamine.

The polysiloxane silicone resin referred to above in the examples is a mixture of polysiloxanes

$$H[OSi(CH_3)_2Si(C_6H_5)_2]_nOH$$

where n is 3–20.

The zinc oxide may be used in a ratio of from less than 0.5:1 up to about 10:1 zinc oxide to binder, although our preferred range is from 1:1 up to 6:1 zinc oxide to binder.

The addition of surfactants improves wettability of the coating and in some instances improves the photographic characteristics.

It will be appreciated that sensitizing dyes may be added to the coating composition such as Rose Bengal, fluorescein, and the like. Although our preferred embodiment employs a developer of manganese nitrate and silver nitrate, other developers may be used including a simple solution of thiourea and silver nitrate in water. Inasmuch as the proportions are disclosed in the copending applications referred to above, this information is not believed critical but may be determined by one skilled in the art regarding the proportions and the particular developers which may be desired.

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.

We claim:

1. A zinc oxide photoconductographic coating on a conductive substrate containing .01 to 4.0% by weight based on the zinc oxide content of the coating of an organic amine selected from the class consisting of NR_3 and R_4NX in which the R's may be the same or different radicals selected from the class consisting of hydrogen, $(CH_2)_nNH_2$ in which n may be 2 to 22, $(CH_2CH_2NH)_nH$ in which n may be 1 to 11, and alkyl groups derived from fatty acids having 1 to 22 carbon atoms, and X is a halide.

2. A photoconductographic element comprising a conductive support having coated thereon a composition containing 40 to 11% by weight of a copolymer of butadiene and styrene, 5 to 1.4% by weight of a silicone resin, 5 to 1.4% by weight of a hydrocarbon thermoplastic terpene resin, 50 to 86% by weight zinc oxide, and .01 to 4.0% by weight based on the zinc oxide content of the coating of an organic amine selected from the class consisting of NR_3 and R_4NX in which the R's may be the same or different radicals selected from the class consisting of hydrogen, $(CH_2)_nNH_2$ in which n may be 2 to 22, $(CH_2CH_2NH)_nH$ in which n may be 1 to 11, and alkyl groups derived from fatty acids having 1 to 22 carbon atoms, and X is a halide.

3. A photoconductographic element described in claim 2 having an aluminum conductive support.

4. A photoconductographic element described in claim 2 having a glass conductive support.

5. A photoconductographic element comprising a conductive support having coated thereon a composition containing 14 to 50% by weight of an organic polymeric binder, 50 to 86% by weight zinc oxide, and .01 to 4.0% by weight based on the zinc oxide content of the coating of an organic amine selected from the class consisting of NR_3 and R_4NX in which the R's may be the same or

different radicals selected from the class consisting of hydrogen, $(CH_2)_nNH_2$ in which n may be 2 to 22, $(CH_2CH_2NH)_nH$ in which n may be 1 to 11, and alkyl groups derived from fatty acids having 1 to 22 carbon atoms, and X is a halide.

6. A photoconductographic element comprising a conductive support having coated thereon a composition containing 40 to 11% by weight of a copolymer of butadiene and styrene, 50 to 86% by weight zinc oxide, and .01 to 4.0% by weight based on the zinc oxide content of the coating of an organic amine selected from the class consisting of NR_3 and R_4NX in which the R's may be the same or different radicals selected from the class consisting of hydrogen, $(CH_2)_nNH_2$ in which n may be 2 to 22, $(CH_2CH_2NH)_nH$ in which n may be 1 to 11, and alkyl groups derived from fatty acids having 1 to 22 carbon atoms, and X is a halide.

7. A photoconductographic element comprising a conductive support having coated thereon a composition containing 40 to 11% by weight of a copolymer of vinyl chloride and vinyl acetate, 50 to 86% by weight zinc oxide, and .01 to 4.0% by weight based on the zinc oxide content of the coating of an organic amine selected from the class consisting of NR_3 and R_4NX in which the R's may be the same or different radicals selected from the class consisting of hydrogen, $(CH_2)_nNH_2$ in which n may be 2 to 22, $(CH_2CH_2NH)_nH$ in which n may be 1 to 11, and alkyl groups derived from fatty acids having 1 to 22 carbon atoms, and X is a halide.

8. A coating composition comprising dry basis 40 to 11% by weight of a copolymer of butadiene and styrene, 5 to 1.4% by weight of a silicone resin, 5 to 1.4% by weight of a hydrocarbon thermoplastic terpene resin, 50 to 86% by weight zinc oxide, and .01 to 4.0% by weight based on the zinc oxide content of the coating of an organic amine selected from the class consisting of NR_3 and R_4NX in which the R's may be the same or different radicals selected from the class consisting of hydrogen, $(CH_2)_nNH_2$ in which n may be 2 to 22 $(CH_2CH_2NH)_nH$ in which n may be 1 to 11, and alkyl groups derived from fatty acids having 1 to 22 carbon atoms, and X is a halide.

9. A coating composition as described in claim 2 in which the coating layer contains a dyestuff sensitizer.

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