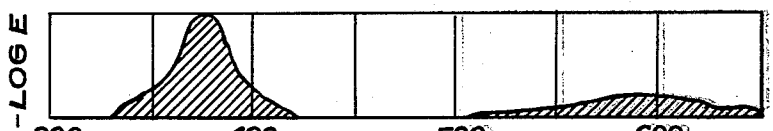
July 27, 1965 N. W. BLAKE ETAL 3,197,307
SURFACE MODIFICATION OF ZINC OXIDE AND
ELECTROPHOTOGRAPHIC MEMBER THEREFROM
Filed Sept. 22, 1964

Fig. 1



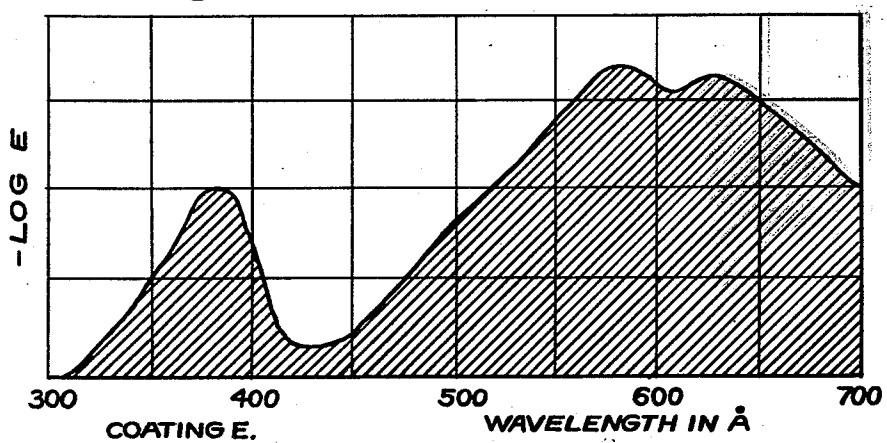
COATING A.
ACTION SPECTRUM OF COATING MADE WITH UNMODIFIED ZnO

Fig. 2



COATING B.
ACTION SPECTRUM OF COATING SENSITIZED WITH UNMODIFIED ZnO

Fig. 3



COATING E.
ACTION SPECTRUM OF COATING SENSITIZED WITH CRYSTAL VIOLET, MADE WITH MODIFIED ZnO

NOTE: CROSS HATCHED AREA IS AREA DISCHARGED UNDER TEST. EXPOSURE (IDENTICAL IN EACH CASE).

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SURFACE MODIFICATION OF ZINC OXIDE AND ELECTROPHOTOGRAPHIC MEMBER THEREFROM

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This application is a continuation-in-part of application Serial No. 75,753, filed December 14, 1960, now abandoned.

This invention is concerned with novel photoconductive substances formed by chemically modifying the surface of zinc oxide. Photoconductivity of zinc oxide is the basis of its use in a number of useful processes, such as photoconductography, xerography, photosensitive cells, and the like.

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

Xerography is described in U.S. Patent 2,297,691, Carlson and others. In one embodiment of the xerographic process, described in British Patent 811,165, a photoconductive layer containing zinc oxide or a similar material in a suitable resinous binder is provided with an electrostatic charge and then exposed to a light image in a manner similar to that employed with ordinary silver halide photographic material. The charge is dissipated in the areas where the light strikes the zinc oxide-resin coating. Subsequently, a colored toner powder is caused to adhere to the surface by electrostatic attraction in those areas which have not been exposed to the light and in which residual charge remains.

In the xerographic process, certain physical properties of the zinc oxide coatings are important for successful operation. In particular, some of these properties are as follows:

(1) The relative effectiveness of different wavelengths of incident light in discharging the coating when a sensitizing dye is added to the zinc oxide dispersion.

(2) The relative efficiency with which radiant energy absorbed by the zinc oxide discharges the coating, and

(3) The ability of the coating to hold an applied electrostatic charge in the dark.

These properties determine the utility of the coating. One (1) and two (2) taken together determine the photographic speed of the coating; that is, they determine the amount of exposure to a given source of light necessary for image formation.

Three (3) determines whether or not the coating is useful in xerography; the coating must retain the charge long enough in the dark to permit image exposure and development.

The above three properties are considered in order below.

(1) This property is usually determined by measuring the action spectrum of a given coating. Unsensitized zinc oxide produces coating with action spectra showing a maximum at about 390 millimicrons and falling rapidly on either side so that light of 410 millimicrons and higher

wavelengths produces little or no discharge. This dependence of such coatings upon light primarily in the ultraviolet part of the spectrum for their photographic activity seriously limits their usefulness since they cannot be exposed with visible light. Since commonly used sources such as tungsten light are much poorer in energy in the ultraviolet range than in the visible portion of the spectrum, exposure times of these coatings using such sources are relatively long.

It has been found that the action spectra of zinc oxide coatings may be extended by the addition of certain dyes to the zinc oxide dispersion. The resulting area of the visible spectrum encompassed by the action spectrum of coatings incorporating dyes is found in practice to be directly related to the absorption spectrum of the dye used. However, not all dyes work equally well. In fact, with conventional zinc oxide, dyes fall clearly into two classes, those which sensitize appreciably and those which sensitize only very slightly or not at all.

If a dye appreciably sensitizes a coating, then when the dye is present in the coating at a concentration of 10^{-6} mole/gram of zinc oxide, the action spectrum of the coating will show that light of wavelength corresponding to that most strongly absorbed by the dye is at least 20% as effective as light absorbed directly by zinc oxide (at a wavelength of 380 millimicrons) in discharging the coating. Each of a very large number of dyes belonging to all common and generic classes has been categorized according to this definition. It has been found previously that only those dyes which contain one or more of the following groups will appreciably sensitize coatings based on conventional zinc oxide: a carboxylic acid group, an aromatic hydroxy group or an aromatic thiol group.

Studies of the partition of dyes between the zinc oxide surface and the binder for the zinc oxide, show that only dyes containing the above groups absorb appreciably to the zinc oxide surface.

The limited number of effective dyes available includes certain dyes of the phthalein class, such as Rose Bengal and fluorescein, and certain substituted cyanine dyes. Even these dyes are not fully adsorbed to the zinc oxide. Moreover, each of these dyes encompasses only a relatively narrow region of the spectrum. Therefore, these limitations have prevented the full realization of the speed of the process when using tungsten illumination, have required the use of multiple dyes to extend the action spectrum throughout the visible (with concomitant difficulties in manufacture because of the varying solubility characteristics of the different dyes) and have generally led to the production of highly colored coatings with relatively low-speed to tungsten light sources.

(2) Changes in the relative efficiency with which light energy absorbed by the zinc oxide discharges the coatings result in proportionate changes in the speed of these coatings. Inability to change this efficiency has limited the applications of these coatings.

(3) It is valuable to be able to change the dark decay that is, the rate at which applied electrostatic charge is lost in the absence of light. Certain coatings have been unsuitable for customary use because of too rapid dark decay. These coatings have been those which contain a high concentration of sensitizing dye. This increase in dark decay, as the concentration of sensitizing dye is increased, critically limits the speed that can be achieved through optical sensitization.

We have discovered new, modified zinc oxides which permit (1) the optical sensitization of the zinc oxide coat-

ing with nearly any dye, (2) changing the above described efficiency of these coatings (either increasing or decreasing it), and (3) changing the dark decay.

One object of this invention is to provide zinc oxide whose surface is chemically reacted with compounds to improve its use for electrophotographic purposes. Another object is to provide a process for modifying zinc oxide to improve its electrophotographic properties. An additional object is to provide a chemically modified zinc oxide which enables zinc oxide coatings to be sensitized with a great number of dyes. Still another object is to provide chemically modified zinc oxides allowing the preparation of coatings in which the above described efficiency is changed. A further object is to provide chemically modified zinc oxides allowing the preparation of coatings in which the dark decay can be changed.

The above objects are obtained by chemically modifying zinc oxide of 98 or higher percent chemical purity by attaching the following entities to a specified percent of its surface:

(a) One or more Lewis acids attached to 10 to 100% of the surface of the zinc oxide. Typical Lewis acids include HCl, zinc chloride, acetyl chloride, sulfur dioxide, sulfur trioxide, sulfuric acid, hydrogen bromide, boron fluoride, hydrogen bromide, acid bromides and chlorides, chlorosilanes, and the like. Lewis acids are described in "The Electronic Theory of Acids and Bases," by W. F. Ludern and S. Zuffanti, John Wiley and Sons, Inc., New York, 1946, pages 15–17 and 43–46. It is understood, of course, that these Lewis acids are not dyes.

Among Lewis acids which may be used are the following: hydrogen sulfide, hydrogen chloride, hydrogen fluoride, hydrogen bromide, sulfuric acid, phosphoric acid, sulfur dioxide, sulfur trioxide, aluminum chloride, boron fluoride, zinc chloride, zinc bromide, thionyl chloride, acetyl chloride, acetyl bromide, trifluoroacetic acid, iodoacetic acid, thioglycolic acid, benzoyl chloride, adipyl chloride, adipyl bromide, terephthaloyl chloride, isophthaloyl chloride, maleic anhydride, silicon tetrachloride, trichloromethylsilane, dichlorodimethylsilane, chlorotrimethylsilane, trichlorophenylsilane, dichlorodiphenylsilane, chlorotriphenylsilane, chlorodimethylphenylsilane and chloromethyldiphenylsilane. All other Lewis acids, which are not dyes, are operative and may be used. Particularly useful Lewis acids are those which do not absorb light having a wavelength between 400 and 700 mμ.

(b) One or more of the salts of aluminum, bismuth, chromium, copper, iron, lithium, magnesium, nickel, tin and titanium attached to 10 to 100 percent of the zinc oxide surface, and

(c) Any of a number of different reducing agents such as tannic acid, gentisic acid, pyrogallol, benzylaminophenol, ascorbic acid, stannous salts, and the like, having in common that they are at least as powerful reducing agents as stannous ion, attached to 0.1 to 20 percent of the zinc oxide surface.

Compositions provided in group (a) are useful in the preparation of electrophotographic coatings, for instance, xerographic coatings. Coatings prepared from them show greatly increased effectiveness of optical sensitization by dye surmounting the limitations mentioned in (1) above. Coatings from them show doubling of the efficiency, defined in (2) above. They also show much decreased rate of dark decay of the applied electrostatic charge, particularly at high concentrations of dye, overcoming the limitations described in (3) above.

Compositions provided in group (b) are useful in the preparation of xerographic coatings. For instance, coatings may be prepared from these compositions for which the efficiency, defined in (2) above, is decreased by a factor of 3 or more.

Compositions provided in group (c) are useful in the preparation of xerographic coatings. For instance, through their use coatings having greatly increased rates of dark decay of applied electrostatic charge may be prepared.

The majority of modifiers fall into a single category, (a), (b), or (c). When a particular modifier falls into category (c) and any of the others, the effect obtained from compositions provided in group (c) predominates. When a modifier falls into (a) and (b), the effect obtained from compositions of group (b) predominates.

In our preferred embodiment, zinc oxide of 98 or higher percent chemical purity is slurried into a chemically inert solvent, such as toluene, the final composition being between 5 and 45 percent zinc oxide. Sufficient modifying chemicals to react with the desired percentage of the surface of the zinc oxide is dissolved separately in a relatively small quantity of solvent such as acetonitrile, dimethylformamide, methanol or toluene. The zinc oxide slurry is agitated violently, such as through the use of a Waring Blendor, while the modifier solution is added dropwise over a period of minutes. After addition of the modifier is complete, other addenda, such as polymer(s) and dye(s) may be added to the slurry, and coatings prepared. Another preferred method is useful when the modifier can be vaporized, for instance, when using a modifier such as hydrogen chloride or $(CH_3)_3SiCl$. In this method, dry zinc oxide powder is stirred rapidly in an enclosed vessel, to which the modifier vapor is slowly added over a period of minutes. Vaporization can be accelerated by heating or by reducing pressure, or by a combination of these two steps. Saturating a stream of inert gas with vapor of the treating chemical and causing it to flow in contact with the zinc oxide is also a means of accomplishing the desired effect. The resulting modified zinc oxide may then be used to prepare electrophotographic coatings in any of the conventional ways.

In many instances, the modifier reacts with the zinc oxide vigorously, and may react with more than just the surface. In the event that the reaction is not controlled carefully, the zinc oxide may become a mixture of unmodified and overmodified zinc oxide which would not be as useful for electrophotographic purposes. The unmodified and the overmodified would both have inferior properties to that of the properly modified zinc oxide. Accordingly, highly reactive modifiers such as hydrogen chloride and acid chlorides must be added to the zinc oxide so that equal exposure of each of the zinc oxide particles to the modifier solution occurs. This is accomplished by continuously and rapidly agitating the zinc oxide with the addition of the modifier at a low rate of addition.

The amount of modifier necessary to react with the desired percentage of the surface depends upon the area of the surface of the particular zinc oxide being treated. Surface area data may be obtained from the manufacturer of the zinc oxide or the surface area may be measured by the known method of nitrogen adsorption.

In order to compare the properties obtained using zinc oxide modified according to our invention, practical methods have been used to measure the properties described above as (1), (2) and (3).

(1) The relative effect of various wavelengths of incident radiation in discharging a zinc oxide coating is determined by exposing a charged coating of dimensions X by Y to a spectrum of radiation, said spectrum changing wavelengths along the X direction and being subject to stepwise intensity attenuation along the Y direction (log of exposure) at each wavelength. Subsequent toning of the sample defines a curve, the spectral response curve of the sample, indicating the effectiveness of various wavelengths of light in discharging the sample. This curve is called the action spectrum of the sample. The spectral distribution of energy of the source producing the spectrum will affect the shape of this curve. However, in practice, a known source, a tungsten filament lamp operated at 3000° K., so that its spectral distribution remains con-

stant, is used. This permits comparison between various action spectra.

Conventional, undyed zinc oxide produces coatings with action spectra as shown in FIGURE 1, Coating A, of the attached drawing, showing a maximum at about 380 millimicrons and falling rapidly on either side, so that light of 410 millimicrons and higher wavelengths produces little or no discharge. FIGURE 2, Coating B, shows the action spectrum of a coating made with unmodified zinc oxide sensitized with Crystal Violet. FIGURE 3, Coating E, shows the action spectrum of a coating made with modified zinc oxide sensitized with Crystal Violet. In each instance, 5×10^{-7} mole of Crystal Violet per gram of zinc oxide was used for the sensitizing agent. The zinc oxide was modified as described in Example 1, using a modifier from group (a) above.

(2) The relative efficiency of radiant energy absorbed by the zinc oxide in discharging zinc oxide coatings is derived from measurements of the relative speeds of the coatings. The speed of a coating depends upon two factors: How much of the incident radiant energy the coating absorbs and how efficiently the absorbed radiation is used to discharge the coating. Intercomparison of the speed values of two different coatings having identical absorption spectra, determines the efficiency of one with respect to the other.

Changes in the relative efficiency of absorbed light energy in discharging the coatings will result in proportionate changes in the speeds of the coatings. For certain applications (e.g., exposure with illuminants of low intensity), it is necessary to have the speed as great as possible and increases in the relative efficiency of the process are desirable. In other applications, very low speed is needed (e.g., for handling in room light) and decreases in the relative efficiency of the process are wanted. Thus, the ability to change this efficiency through the use of modified zinc oxide extends the range of application of zinc oxide coatings.

The speed of xerographic coatings is measured as follows:

A coating is charged in the dark and mounted in a sensitometer, immediately behind a transparency of stepwise-increasing neutral density. Each step in this transparency attenuates the light reaching the surface of the coating by approximately 25 percent more than the preceding step. The most transparent step allows 19 footcandles of illumination, from a 3000° K. tungsten source, to strike the sample. The sample is exposed in the sensitometer for 3 seconds and toned in a standard fashion. The first step of the toned sample to which no toner is held indicates the speed of the sample. Since speed is relative, the speed number associated with the most transparent step of the scale is arbitrarily placed at 20. Succeeding steps have speed numbers of 25, 31, 39, 49, 61, and so forth. The higher the number, the faster the speed, and the more dense the step; that is, the less light used to discharge the sample. On this scale, unsensitized zinc oxide coatings, prepared in a standard fashion, have a speed of approximately 60. Accuracy is within about 25 percent or one step.

(3) The ability of zinc oxide coatings to hold an applied electrostatic charge in the dark is determined by charging a sample and observing its surface potential, as a function of time, in the dark. Measurement is started immediately after charging and continued for 3 minutes. The potential immediately after charging and at ½, 1, 2 and 3 minutes after charging is noted. Frequently, the time necessary for the initial potential to drop to half of its value is also noted.

It is desirable to be able to change the rate at which applied electrostatic charge is lost in the absence of light. In some applications it is important to reduce this rate. Thus, xerographic utility of zinc oxide coatings requires that they hold an appreciable fraction of an applied charge in the dark for a period of time equal to that necessary to expose and tone such coatings. If longer than 3 minutes is required for the initial potential to drop to half-value, charge retention of the coating is adequate.

Unsensitized conventional zinc oxide coatings require longer than 3 minutes for the initial potential to drop to half-value, when the applied electrostatic charge is negative. If the applied electrostatic charge is positive, the potential of the surface drops to half-value in less than 15 seconds. Thus, such coatings are difficult or impossible to use with positive charging even though this polarity of charging is desirable in certain applications. With dye-sensitized coatings, it has been observed that the greater the concentration of dye in the coating the more rapid the dark decay of charge. At very high dye levels, even with negative charging, the dark decay is frequently so rapid the coating is useless for xerographic purposes. The data in Table V illustrates this. The increase in dark decay as the dye concentration is increased thus effectively limits the speed achievable through optical sensitization, as it limits the amount of dye that can be used.

In the practice of this invention, the particle size of the zinc oxide which may be used may be from 0.01 micron to 5.0 microns. Surface modification does not require zinc oxide of any particular size; the size requirement of zinc oxide particles depends upon their ability to be dispersed in a given binder for electrophotographic purposes. For instance, any zinc oxide of a size which can be used for electrophotographic purposes can be surface modified within the scope of our invention, to obtain the improved characteristics described herein.

In order to provide a coating for electrophotographic purposes, modified zinc oxide may be dispersed in a polymeric coating of various types in a ratio of 0.5 to 6 parts of modified zinc oxide to about one part of an organic polymeric binder such as a cellulose ester, polymers derived from styrene and butadiene, polystyrene, polyvinyl chloride, polyvinylacetals, poly-n-butylmethacrylate, polyolefins, polyesters, polyamides, and the like. The only requirement for the binder for xerographic use is that coatings of it, free from zinc oxide, be capable of holding an applied electrostatic charge. Suitable coatings have a dielectric constant of about 9–2.5. These coatings may contain 0.1×10^{-7} to 50×10^{-7} mole of dye per gram of zinc oxide. Any type of dye may be used.

The following examples are intended to describe our invention but are not intended to limit it in any way.

EXAMPLE 1

168 grams of zinc oxide were added to 238 grams of xylene in a water-jacketed Waring Blendor. The particle size of the zinc oxide most frequently occurring was 0.1 micron and 90% of the particles were less than 0.4 micron. Sixty milliliters of xylene, in which the Lewis acid SO_2 was dissolved, were then added dropwise, with thorough mixing. The slurry was then stirred for 10 minutes, at the end of which time 8.4×10^{-5} mole of Crystal Violet dissolved in 15 grams of methanol was added. The mixture was stirred for 5 minutes, then 14.4 grams of a 60% solids solution in toluene of an organopolysiloxane resin was added, followed by addition of 111.9 grams of a 30% solids solution in toluene of a styrene-butadiene polymer. The mixture was then stirred for 3 minutes. At the end of this time, it was coated on paper to give a coverage of 3 grams of dry coating per square foot. Similar coatings were made, as shown below, without modification with the Lewis acid and without the dye. These coatings served as controls. The coatings were conditioned for three days at 50% relative humidity at 70° F. Then the action spectra and speed were determined as described above. These coatings are described and the speed data obtained from them are given in Table I.

Table I

Coating	SO_2		Dye present	Speed
	Moles	Gram		
A	0	0	No	60
B	0	0	Yes	131
C	0.75×10^{-3}	4.8×10^{-2}	Yes	790
D	1.5×10^{-3}	9.6×10^{-2}	Yes	3,400
E	2.25×10^{-3}	14.4×10^{-2}	Yes	4,200
F	3.0×10^{-3}	19.2×10^{-2}	Yes	1,600
G	4.5×10^{-3}	28.8×10^{-2}	Yes	2,000
H	6.0×10^{-3}	28.4×10^{-2}	Yes	393
I	9.0×10^{-3}	57.6×10^{-2}	Yes	192
J	2.5×10^{-3}	14.4×10^{-2}	No	122

Action spectra of Coatings A, B, and E are given in FIGURES 1, 2 and 3.

Optimum sensitization of the dye occurs when 2.25×10^{-3} mole of SO_2 are used for 168 grams of zinc oxide. Based on the reaction $ZnO+SO_2\rightarrow ZnSO_3$, this corresponds to approximately 20 percent of the surface zinc oxide reacted for the sample of zinc oxide used. Thus, the modification of zinc oxide with the optimum amount of SO_2 doubles the speed of the coating, even in the absence of dye. Therefore, the efficiency of the coating is doubled. Reaction of the zinc oxide with SO_2 was determined by tests of the supernatant liquid obtained from centrifuging the slurry after addition of the SO_2 but prior to the addition of the dye. No SO_2 was found to be present.

EXAMPLE 2

The procedure used to prepare coatings C to I of Example 1 was used to prepare a series of coatings from each of the Lewis acids in Table II in place of SO_2. Within each series the amount of modifier used varied from 0.3×10^{-3} to 1×10^{-2} mole. In those cases where the Lewis acid was not sufficiently soluble in xylene, it was dissolved in another suitable solvent such as methanol. The speeds of these coatings were then determined as described above. The amount of modifier with which maximum speed was obtained is given in Table II and is called the optimum amount of modifier.

Coatings were then prepared using the procedure used to prepare coating J of Example 1, but using the above-determined optimum amount of Lewis acid in place of SO_2. In each case, an increase in speed of a factor of 2 was observed.

Table II

THE OPTIMUM AMOUNTS OF VARIOUS LEWIS ACIDS NEEDED TO OPTIMUMLY MODIFY ZINC OXIDE

Lewis acid:	Moles acid/168 g. ZnO
HCl	4.5×10^{-3}
Acetyl chloride	4.5×10^{-3}
Adipyl chloride	2.25×10^{-3}
Cyanuric chloride	2.25×10^{-3}
Phenyl trichlorosilane	1.5×10^{-3}
Dimethyl dichlorosilane	2.25×10^{-3}
Trimethyl chlorosilane	4.5×10^{-3}
HF	4.5×10^{-3}
Zinc chloride	2.25×10^{-3}
So_3	2.25×10^{-3}
Sulfamic acid	4.5×10^{-3}

In each instance, reaction occurred between the modifier and zinc oxide. No modifier could be detected in the supernatant liquid obtained from centrifuging the slurry after addition of the modifier but prior to the addition of dye.

EXAMPLE 3

The procedure of Example 1 with 4.5×10^{-3} mole of hydrogen chloride as modifier, replacing the SO_2 of Example 1, and 5×10^{-7} mole of dye per gram of zinc oxide was used to prepare coatings from the dyes listed below in Table III. Coatings were also prepared using unmodified zinc oxide. In certain cases the percent of the added dye adsorbed to the zinc oxide was determined, by measuring the amount of dye present in the supernatant liquid produced by centrifuging the slurry. Action spectra of the coatings prepared from modified zinc oxide showed sensitivity in the wavelength region of light absorbed by the dye, in accordance with increased speeds as shown in Table III. Action spectra of the coatings prepared from unmodified zinc oxide showed little or no sensitivity in the spectral range of light absorbed by the dye, except for the blue-red cyanine dye and the dyes fluorescein and Rose Bengal, each of which has either a —COOH or an aromatic —OH group attached to it.

Table III

OPTICAL SENSITIZATION OF ELECTROPHOTOGRAPHIC COATINGS BASED ON EITHER MODIFIED OR UNMODIFIED ZINC OXIDE

Dye	Type	Modified ZnO		Unmodified ZnO	
		Percent dye on ZnO	Speed	Percent dye on ZnO	Speed
Blue-red cyanine	Cyanine	99	4,250	70	2,030
Quinaldine Red	do	90	2,620	20	204
Malachite Green	Triphenylmethane	60	995	(2)	67
Lithosol Blue 6G	do	(1)	2,620	(2)	83
Crystal Violet	do	75	4,250	(2)	131
Amanil Black ROL	Azo	(1)	164	(2)	43
p-Methyl Red	do	(1)	250	(2)	23
"Pontacyl" Blue-Black Sx	do	(1)	204	(2)	67
Nigrosine	do	(1)	204	(2)	17
Chrysoidine 4	do	(1)	164	(2)	43
Methylene Blue	Thiazine	90	4,250	(2)	104
Chrome Blue GCB	Oxazine	(1)	500	(2)	131
Phenosafranin	Azine	90	995	(2)	131
1, 4-diaminoanthraquinone	Anthraquinone	25	250	(2)	83
D & C Violet #2 base	do	(1)	164	(2)	23
Alizarin	do	50	315	(2)	204
Celanthrene Red	do	(1)	164	(2)	55
Fluorescein	Phthalein	100	791	50	315
Rhodamine B	do	(1)	3,380	(2)	500
Rose Bengal	do	90	995	60	627
Phosphine RN	Acridine	(1)	500	(2)	104
Acridine Orange	do	(1)	627	(2)	83
Naphthol Yellow S	Nitro	(1)	104	(2)	43
Auramine O	Diphenyl methane	(1)	627	(2)	55
Thioflavine TG	Thiazole	(1)	500	(2)	67

[1] Appreciable dye adsorbed. [2] Little or no dye adsorbed.

EXAMPLE 4

The procedure of Example 1 was used to prepare the coatings of Table IV below replacing the SO_2 of Example 1 with the modifier listed in Table IV. Dye was not added to any of the coatings of Table IV in order that speed measurements could be used as efficiency measurements. In those instances where the modifier of Table IV was not entirely soluble in xylene, a solvent such as methanol, acetonitrile, or dimethylformamide was substituted.

Table IV

DECREASE PHOTOCONDUCTIVITY

Modifier	Concentration mole/56 g. ZnO	Speed
$CuCl_2$	1×10^{-3}	20
SnI_4	1×10^{-4}	20
CuCl	1×10^{-4}	20
BiI_3	1×10^{-4}	31
$NiCl_2$	2×10^{-3}	31
$MgCl_2$	1×10^{-3}	34
Tetraiospropyl titanate	1×10^{-3}	20
SnI_2	1×10^{-4}	20
LiCl	1×10^{-3}	39
$CrCl_3$	1×10^{-3}	31
$FeCl_3$	1×10^{-3}	31
$AlCl_3$	1×10^{-3}	39

The data in Table IV show that modification for these compounds decreases the efficiency with which radiation, absorbed by the zinc oxide, causes discharge of the coating.

EXAMPLE 5

224 grams of zinc oxide were sealed in a vessel provided with a stirrer capable of tumbling the dry powder over upon itself rapidly. 200 ml. of gaseous hydrogen chloride at atmospheric pressure and at 20° C. were introduced slowly into the vessel. After addition of the hydrogen chloride, a solution of 317.1 grams of toluene, 20.9 grams of methanol and 0.03 gram of Crystal Violet dissolved in about 10 ml. of methanol were added. The resulting mixture was dispersed in a high shear mixer for 10 minutes. Twelve grams of a 60 percent solids solution in toluene of the organopolysiloxane resin was added and dispersed for one more minute. Finally, 96 grams of a 30 percent solids solution in toluene of a styrene-butadiene copolymer was added and mixed for another 2 minutes. The dispersion was then coated on a paper support and the resulting xerographic printing paper had a speed of 5300. In other identical tests, the speeds of the coatings ranged from 3400 to 5300.

EXAMPLE 6

Zinc oxide was treated with hydrogen chloride, as described in Example 5. One portion of the zinc oxide was immediately blended with solvent, polymers and dye and coated as described. The resulting speed of the coating was 2600.

After three days a second portion of the modified zinc oxide was compounded and coated in the same manner. The speed of this coating was again 2600.

After seven days, the third portion of the modified zinc oxide was compounded and coated in the same manner. The speed of this coating was 2000. This value is only approximately 20% less than the 2600 obtained and is within the experimental limits of the general results obtained in the process.

EXAMPLE 7

The procedure of Example 1 was used to prepare the coatings of Table V below. 4.5×10^{-3} moles of acetyl chloride were used as modifier in place of the SO_2 for the coatings based on surface-modified zinc oxide. A blue-red cyanine dye was used to sensitize, in each case. Coatings from unmodified zinc oxide gave poor dark decay characteristics at high dye levels. The use of modified zinc oxide gives increased speed and the dark decay is not adversely affected at high dye levels.

Table V

EFFECT OF SENSITIZATION LEVEL ON DARK DECAY OF ELECTROSTATIC CHARGE USING COATINGS BASED ON (a) UNMODIFIED AND (b) MODIFIED ZnO

Moles of blue-red cyanine dye/g. of ZnO	Speed	V_0	$V_{1/2}$	V_3	$T_{V/2}$
(a) 5×10^{-7}	995	580	470	310	
(b) 5×10^{-7}	1,615	395	325	215	
(a) 10×10^{-7}	2,030	600	480	---	2¼ min.
(b) 10×10^{-7}	3,380	420	390	340	
(a) 25×10^{-7}	2,620	370	220	---	¾ min.
(b) 25×10^{-7}	8,680	300	270	180	

V_0 is the initial potential (in volts) of the applied electrostatic charge.
$V_{1/2}$ is the potential (in volts) of the applied electrostatic charge, after ½ minute in the dark.
V_3 is the potential of the applied electrostatic charge, after decayed for 3 minutes in the dark.
$T_{V/2}$ is the time (in minutes) necessary for the applied electrostatic charge to decay to half of its initial potential.

EXAMPLE 8

168 grams of zinc oxide were added to 238 grams of commercial xylene in a water-jacketed quart Waring Blendor jar, and 60 ml. of xylene containing 4.5×10^{-3} equivalents of hydrogen chloride were added slowly with thorough mixing. The slurry was mixed for 10 minutes, at the end of which time 5.1 grams of methanol containing 0.02345 gram of p-methyl red and 0.0137 gram of Crystal Violet were added and the mixture stirred for 5 minutes. Then, 14.4 grams of an organopolysiloxane solution, 60 percent solids in toluene, was added, and the mixture stirred for one minute. At the end of this time 111.9 grams of a styrene-butadiene copolymer, 30 percent solids in toluene, was added and the mixture stirred for 2 minutes. The mixture was then coated on paper and dried. Its speed is 2600.

The above procedure, omitting the hydrogen chloride addition, yields a coating with a speed of 100 or less.

EXAMPLE 9

2017 grams of toluene and 35 grams of methanol were mixed in a gallon Waring Blendor. 2057.4 grams of zinc oxide were added over a 45-minute period. The blender was water-jacketed at 100° F. (a) 154 grams of this slurry were transferred to a pint Waring Blendor; 4 grams of methanol were added followed by 54 grams of a 33⅓ percent solution of the resins comprising 80 parts of styrene-butadiene copolymer solution, 60 percent solids in toluene and 10 parts of organopolysiloxane solution, 30 percent solids in toluene, and 10 parts of Piccopale hydrocarbon resins. The slurry was stirred 5 minutes and then coated onto aluminum foil. (b) The remainder of the zinc oxide slurry in the gallon Waring Blendor was surface-modified using 2,864 ml. of gaseous HCl. 154 grams of this slurry of surface-modified zinc oxide were then treated as in (a) above.

A sample of each of the two coatings thus made was exposed for 10 seconds, to 400 foot candles of tungsten illumination incident upon a photographic step tablet in contact with the photoconductive surface. The conductivity pattern induced by this exposure was then developed to a visible image by an essentially two-step process (the first electrolytic, the second chemical) in the following way:

A cellulose sponge saturated with an aqueous solution of 1.0% manganous nitrate was drawn several times across the surface of the exposed photoconductographic surface, the sponge being held at a 60-volt positive potential with respect to the aluminum foil backing of the photoconductive layer. The layer surface was then dried with an absorbent tissue. The image material, deposited by this electrolytic step was then rendered visible by treatment with a 5% by weight silver-nitrate solution, after which the print surface was rinsed with water and blotted dry.

The photoconductographic paper containing the modified zinc oxide was two to four times faster in photographic speed than the paper containing unmodified zinc oxide.

EXAMPLE 10

Use of a base, e.g. potassium hydroxide: 56 grams of zinc oxide were treated with 2×10^{-3} moles of KOH in methanol. The zinc oxide so treated, in a binder, was coated out. The coating had a V_0 of 30 volts and a τ

$$\left(\text{or } \frac{T_v}{2}\right)$$

of 30 seconds. A similar coating from zinc oxide not treated with KOH had a V_0 of 500 volts and a

$$\frac{T_v}{2} \text{ of} > 3 \text{ minutes.}$$

EXAMPLE 11

Use of a chelating agent, e.g. hexamethylenediamine: 56 grams of zinc oxide were treated with 2×10^{-3} moles of hexamethylenediamine in methanol. The resulting zinc oxide was then treated with 1×10^{-6} moles of Rose Bengal dye per gram of zinc oxide (10X). The zinc oxide so treated, in a binder, was coated out. The coating had a speed of 1252, V_0 of 260 volts, and a

$$\frac{T_v}{2}$$

of 45 seconds. In the absence of treatment with hexamethylenediamine, a similar coating had a speed of 1252, V_0 of 550 volts and a

$$\frac{T_v}{2} \text{ of} > 3 \text{ minutes.}$$

Photoconductive zinc oxide referred to herein is intended to be zinc oxide which may be prepared by various methods including the French process, the wet process, the American process and the like, provided it is at least 98% pure. Typical methods of preparing zinc oxide are referred to in "A Volume-Charge Capacitor Model for 'Electrofax' Layers," J. A. Amick, RCA Review, vol. 20, 770–784, December 1959. The particular method of preparing the zinc oxide is not limiting to our invention providing the zinc oxide is photoconductive in nature.

The units expressed herein have been based on grams of zinc oxide for convenience. It will be appreciated that the range of proportions can be expressed as 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide or 1.8×10^{-8} to 9.0×10^{-5} mole of modifier per gram of zinc oxide.

By conducting substrates are intended electrically conducting glass, zinc, aluminum and similar metallic substances, resinous materials having conductors incorporated therein to render them conductive, polymeric materials having metallic coatings thereon, and the like.

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. Finely divided photoconductive zinc oxide of improvide dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with a Lewis acid stronger than zinc oxide.

2. Finely divided photoconductive zinc oxide of improved dye absorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with aluminum chloride.

3. Finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particlse, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with SO_2.

4. Finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with HCl.

5. Finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with acetyl chloride.

6. Finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with hexamethylenediamine.

7. A photographic element for use in electrostatic photographic processes comprising 30–90% of a photoconductive finely divided zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with a Lewis acid stronger than zinc oxide, said zinc oxide dispersed in an insulating film-forming medium and coated on a non-conducting substance.

8. A photographic element for use in electrostatic photographic processes comprising 30–90% of photoconductive zinc oxide containing on at least 10% of the surface of the zinc oxide of improved dye adsorption particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with aluminum chloride, dispersed in an insulating film-forming medium and coated on a non-conducting substrate.

9. A photographic element for use in electrostatic photographic processes comprising 30–90% of photoconductive zinc oxide containing on at least 10% of the surface of the zinc oxide of improved dye adsorption particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with SO_2, dispersed in an insulating film-forming medium and coated on a non-conducting substrate.

10. A photographic element for use in electrostatic photographic processes comprising 30–90% of photoconductive zinc oxide containing on at least 10% of the surface of the zinc oxide of improved dye adsorption particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with HCl, dispersed in an insulating film-forming medium and coated on a non-conducting substrate.

11. A photographic element for use in electrostatic photographic processes comprising 30–90% of photoconductive zinc oxide containing on at least 10% of the surface of the zinc oxide of improved dye adsorption particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with acetyl chloride, dispersed in an insulating film-forming medium and coated on a non-conducting substrate.

12. A photographic element for use in electrostatic photographic processes comprising 30–90% of photoconductive zinc oxide containing on at least 10% of the surface of the zinc oxide of improved dye adsorption particles, a modifier in the concentration of 0.14×10^{-5} to

7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with hexamethylenediamine, dispersed in an insulating film-forming medium and coated on a non-conducting substrate.

13. A photographic element for use in photoconductographic processes comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with a Lewis acid stronger than zinc oxide, dispersed in an insulating film-forming medium, and coated on a conducting substrate.

14. A photographic element for use in electrostatic photographic processes comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with aluminum chloride, dispersed in an insulating film-forming medium and coated on a conducting substrate.

15. A photographic element for use in electrostatic photographic processes comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with SO_2, dispersed in an insulating film-forming medium and coated on a conducting substrate.

16. A photographic element for use in electrostatic photographic processes comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zince oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with HCl, dispersed in an insulating film-forming medium and coated on a conducting substrate.

17. A photographic element for use in electrostatic photographic processes comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with acetyl chloride, dispersed in an insulating film-forming medium and coated on a conducting substrate.

18. A photographic element for use in electrostatic photographic processes comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide particles, a modifier in the concentration of 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, obtained by reacting the zinc oxide with hexamethylenediamine, dispersed in an insulating film-forming medium and coated on a conducting substrate.

19. A photographic element for use in an electrostatic photographic process comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, containing a dye adsorbed to the zinc oxide, dispersed in an insulating film-forming medium and coated on a non-conducting substrate, said modifier obtained by reacting zinc oxide with a Lewis acid stronger than zinc oxide.

20. A photographic element for use in an electrostatic photographic process comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, containing a dye adsorbed to the modified zinc oxide, dispersed in an insulating film-forming medium and coated on a non-conducting substrate, said modifier obtained by reacting zinc oxide with aluminum chloride.

21. A photographic element for use in an electrostatic photographic process comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, containing a dye adsorbed to the modified zinc oxide, dispersed in an insulating film-forming medium and coated on a non-conducting substrate, said modifier obtained by reacting zinc oxide with SO_2.

22. A photographic element for use in an electrostatic photographic process comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, containing a dye adsorbed to the modified zinc oxide, dispersed in an insulating film-forming medium and coated on a non-conducting substrate, said modifier obtained by reacting zinc oxide with HCl.

23. A photographic element for use in an electrostatic photographic process comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, containing a dye adsorbed to the modified zinc oxide, dispersed in an insulating film-forming medium and coated on a non-conducting substrate, said modifier obtained by reacting zinc oxide with acetyl chloride.

24. A photographic element for use in an electrostatic photographic process comprising 30–90% of a finely divided photoconductive zinc oxide of improved dye adsorption containing on at least 10% of the surface of the zinc oxide 0.14×10^{-5} to 7.2×10^{-3} mole of modifier per mole of zinc oxide, containing a dye adsorbed to the modified zinc oxide, dispersed in an insulating film-forming medium and coated on a non-conducting substrate, said modifier obtained by reacting zinc oxide with hexamethylenediamine.

25. A process for improving the dye adsorption of photoconductive zinc oxide comprising contacting finely divided zinc oxide with a Lewis acid stronger than zinc oxide, sufficiently to incorporate on at least 10% of the surface of the zinc oxide 0.14×10^{-5} to 7.2×10^{-3} mole of modified zinc oxide per mole of zinc oxide.

26. A process for improving the dye adsorption of photoconductive zinc oxide comprising contacting the finely divided zinc oxide with a gaseous Lewis acid in order to incorporate on at least 10% of the surface of the zinc oxide 0.14×10^{-5} to 7.2×10^{-3} mole of modified zinc oxide per mole of zinc oxide, obtained by reacting zinc oxide with the gaseous Lewis acid stronger than zinc oxide.

27. A process for improving the dye adsorption of photoconductive zinc oxide comprising contacting the finely divided photoconductive zinc oxide with a surface modifying material in order to incorporate on the surface of the zinc oxide from 0.14×10^{-5} to 7.2×10^{-3} mole of modified zinc oxide per mole of zinc oxide and then adding dye, said modified zinc oxide determined by reacting the zinc oxide with a Lewis acid stronger than zinc oxide.

28. A process for improving the dye adsorption of photoconductive zinc oxide comprising contacting the finely divided photoconductive zinc oxide with a surface modifying material in order to incorporate on the surface of the zinc oxide from 0.14×10^{-5} to 7.2×10^{-3} mole of modified zinc oxide per mole of zinc oxide and then addind dye, said modified zinc oxide obtained by reacting the zinc oxide with aluminum chloride.

29. A process for improving the dye adsorption of

photoconductive zinc oxide comprising contacting the finely divided photoconductive zinc oxide with a surface modifying material in order to incorporate on the surface of the zinc oxide from 0.14×10^{-5} to 7.2×10^{-3} mole of modified zinc oxide per mole of zinc oxide and then adding dye, said modified zinc oxide obtained by reacting the zinc oxide with SO_2.

30. A process for improving the dye adsorption of photoconductive zinc oxide comprising contacting the finely divided photoconductive zinc oxide with a surface modifying material in order to incorporate on the surface of the zinc oxide from 0.14×10^{-5} to 7.2×10^{-3} mole of modified zinc oxide per mole of zinc oxide and then adding dye, said modified zinc oxide obtained by reacting the zinc oxide with HCl.

31. A process for improving the dye adsorption of photoconductive zinc oxide comprising contacting the finely divided photoconductive zinc oxide with a surface modifying material in order to incorporate on the surface of the zinc oxide from 0.14×10^{-5} to 7.2×10^{-3} mole of modified zinc oxide per mole of zinc oxide and then adding dye, said modified zinc oxide obtained by reacting the zinc oxide with acetyl chloride.

32. A process for improving the dye adsorption of photoconductive zinc oxide comprising contacting the finely divided photoconductive zinc oxide with a surface modifying material in order to incorporate on the surface of the zinc oxide from 0.14×10^{-5} to 7.2×10^{-3} mole of modified zinc oxide per mole of zinc oxide and then adding dye, said modified zinc oxide obtained by reacting the zinc oxide with hexamethylenediamine.

No references cited.

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