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3,238,149

METHOD FOR IMPROVING THE PHOTOCONDUCTIVE RESPONSE OF DYE SENSITIZED ZINC OXIDE

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This invention relates to methods of dye-sensitizing zinc oxide, and to the products produced thereby.

The methods and products of the present invention are particularly useful in the electrostatic printing arts.

The general principles of electrostatic printing are well known in the prior art. For example, electrostatic printing processes commonly employ a printing medium comprising a photosensitive pigment, usually finely divided zinc oxide, incorporated in a non-conducting binder vehicle on a suitable base. An electrostatic charge is imparted to such a printing medium by means of a high voltage corona discharge. The charged medium is then exposed to a light image having light and dark portions to be reproduced. Those portions of the charged medium exposed to light become photoconductive and substantially lose their charge. Those portions of the medium not exposed to light retain an electrostatic charge in areas corresponding to the dark portions of the image. This latent electrostatic image on the medium is then developed, commonly by applying a charged dry, fusible particulate pigment over the exposed medium, whereby particles of the pigment are attracted to the electrostatic charge remaining on the unilluminated portions of the exposed medium and visibly reproduce the invisible charge image. Commonly, the image is then fixed in the medium by heating, whereby the finely divided pigment is fused onto the surface of the medium. Alternatively, liquid developing agents containing particles dispersed in a fluid medium can be used for developing.

The prior art process as described has numerous disadvantages. For example, if white printing media are desired, they must be prepared with zinc oxide pigments which become photoconductive only when exposed in a certain limited, high-frequency, spectral range. Satisfactory exposure of such media necessitates the use of light sources having a strong component in the ultra-violet range, such as mercury-vapor lamps. Such light sources are expensive because of their special construction, and are often bulky. Further, devices making use of such sources must be equipped with optical systems transmitting ultra-violet light, adding considerably to the cost of such devices.

The prior art, in attempting to increase the light sensitivity of zinc oxide-containing electrostatic printing media, has developed dye-sensitized media. However, the prior art dye-sensitized media are prepared in a manner said to render the light sensitivity of the media dependent upon the amount of dye employed in the media. Thus, the prior art incorporates a sensitizing dye, together with a zinc oxide pigment, in the binder matrix applied to a suitable base. The resulting product contains a large quantity of dye in the binder, imparting a heavy tint thereto.

The tint of the printing papers produced in the prior art is said to be a forced compromise between the objectionable color imparted by the dye to the paper and the increased sensitivity said to be afforded by increasing amounts of dye. However, it has been found that the presence of large amounts of dye in these media actually decreases their sensitivity, since the excess dye acts as a filter absorbing light which would otherwise be effective in photosensitizing the zinc oxide particles.

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The present invention concerns the production of substantially colorless, white-appearing, dye-sensitized zinc oxide pigments containing no dye in excess of that useful for photosensitization of the zinc oxide pigment. Thus, the applicants have discovered that zinc oxide can be sensitized with such minute amounts of dye as will impart little or no residual tint to printing media prepared from such sensitized pigments. The elimination of excess dye from the media increases their sensitivity by obviating filter effects, and has permitted the development of media having a predetermined desirable photosensitive response, including substantially panchromatic media which are photosensitive over a broad portion of the visible spectrum (i.e. from about 4000 to about 7000 Å.).

Although several theories are current concerning the mechanism of dye sensitization of photosensitive particles, it is believed that such sensitization involves excitation, by light, of electrons into the conduction band of the dye molecule. The electron then drifts into the conduction band of the photoconductor or other photosensitive particle on which the dye molecule is adsorbed. In such a mechanism, excess, unadsorbed, dye does not affect the photosensitivity of the adsorbing particle, and may even be detrimental in reducing the sensitivity of the system by absorbing light which would otherwise reach adsorbed dye molecules.

The dyes employed to sensitize zinc oxide according to the invention are organic materials able to transfer electrons into the conduction band of the oxide when illuminated with light of predetermined spectral characteristics, particularly visible light (e.g. from a tungsten source), thus rendering the oxide photoconductive outside its normal spectral range of response, which normal range is far toward the ultra-violet. This dye-sensitization, which results in the formation of particles of white zinc oxide having organic dye molecules adsorbed thereon, must be distinguished from the sensitization of zinc oxide by conversion of the white oxide to another form, commonly known as "pink" zinc oxide. The latter process involves treatment of pure white zinc oxide with reagents effecting chemical change of the starting material, and is exemplified in the teachings of U.S. Patents 2,727,807 and 2,727,808, among others.

The dyes employed to sensitize zinc oxide according to the invention are colored organic materials, adsorbable on the oxide, which have an absorption peak or peaks outside the ultra-violet spectrum and in the visible spectrum. The dyes are, in general, those heretofore used in the photographic arts for sensitizing silver halides (cf. "The Theory of the Photographic Process" by C. E. Kenneth Mees, the Macmillan Publishing Company, N.Y., Revised Edition (1954)), and include acridine dyes such as Acridine Orange (absorption peak at 4930 Å.), thiazine dyes such as Methylene Blue (absorption peaks at 6678–6093 Å.), phthaline dyes such as Rose Bengal (5600 Å.) and Eosin Y (4700–5600 Å.), cyanine dyes such as Kryptocyanine, and triphenylmethane dyes such as Malachite Green (6320 Å.), Crystal Violet (5910–5405 Å.), and Alphasurine (6000–6500 Å.).

It is believed that maximum sensitization of the dye-treated zinc oxide particles is obtained when a substantially monomolecular layer of the dye has been adsorbed on the surface of the zinc oxide particles. Only the dye thus adsorbed is capable of usefully transferring electrons to the zinc oxide particles: dye in excess of this quantity only interferes by absorbing light otherwise destined for the sensitized particles. The method of sensitizing the particles is, thus, to form such a dye monolayer, and then to remove excess dye from the particles. This method is to be contrasted with the prior art in which large amounts of dye are combined with the par-

ticles to be sensitized in the binder matrix of a printing medium, and are retained in the medium after its preparation.

In forming a monomolecular layer of dye on zinc oxide particles by contacting them with a dye and then removing any dye in excess of that required for the monomolecular dye layer, the sensitizing dyes are suitably applied to the zinc oxide particles to be sensitized by contacting the oxide particles with a solution of the sensitizing dye dissolved in a solvent for the dye. Suitable solvents are known to the art, and include polar solvents such as ethanol, methanol, acetone, and similar liquids having a dielectric constant greater than about 5 at 20° C.

In sensitizing the zinc oxide pigment, it is convenient to prepare a paste of the pigment with a solution of the dye. For example, 70 grams of zinc oxide particles having an average diameter of 3 microns are suitably mixed with 100 cc. of a dye solution having a concentration from between 10^{-5} M to 10^{-2} M. Zinc oxide particles in this state of subdivision have a surface area of about 3450 cm.²/gm., so that in these solutions the ratio of the mols of dye employed to the surface area of the zinc oxide particles being treated varies between about 4×10^{-9} mols/cm.² to about 4×10^{-12} mols/cm.². Particularly good results are obtained when the dye/surface area ratio is kept within this range.

The size of the zinc oxide particle being treated is not limited to that mentioned above. A number of zinc oxide powders are commercially available and are suitable for use in preparation of electrostatic printing media. The particles may range in size from an average particle diameter of about 0.1 μ , having a surface area of about 10×10^4 cm.²/gm. to much larger particles having a surface area of only about 2400 cm.²/gm. Numerous zinc oxide particles of this type are discussed, for example, in the article by Emmett et al., in *Industrial and Engineering Chemistry, Analytical Edition*, 13, 28-33 (1941). In sensitizing zinc oxide materials of the type described, it has been observed that optimum results in the dye sensitization process are suitably achieved when the ratio of the amount of dye contacted with the particles to the surface area of the particles being treated is about 10^{-10} mols/cm.². Although suitable ratios of dye to surface area can be achieved by applying the dye in either dilute or concentrated solution, it has been observed that the dye is better adsorbed on the zinc oxide particles when the dye solutions are relatively concentrated, optimally around 10^{-4} M to 10^{-3} M.

It is desirable to allow the zinc oxide particles to remain in contact with the dye solutions for as long a period of time as is feasible, since adsorption is a time dependent process. At room temperature (25° C.), Rose Bengal and Eosin Y, for example, have been observed to be suitably adsorbed on zinc oxide particles from methanol solution in about 6-24 hours. The application of Methylene Blue or Acridine Orange in acetone is suitably allowed to proceed at room temperature for a period of time ranging from about 24 hours to one week. Sensitization can be achieved with the dyes mentioned if the dye solution and particles are allowed to remain in contact with each other for at least about 24 hours at room temperature.

A preferred method of sensitization, which shortens the time period of contact, proceeds by contacting the dye solution and zinc oxide particles at a temperature above room temperature, for example, at temperatures up to or above 100° C. Temperatures above 100° C. may also be employed providing they are not so high as to cause substantial deterioration of the dye employed. Practically, heating is generally accomplished at a temperature below about 200° C., such as at 150° C., in from 3 to 24 hours in appropriate containers.

The increase in adsorption brought about by use of elevated temperatures can be illustrated by reference to

a treatment of 70 grams of zinc oxide in 100 cc. of a 10^{-4} M solution, in methanol, of Rose Bengal or Eosin Y. At 150° C., adsorption of either of these dyes is substantially complete in 3 hours; that of Methylene Blue is substantially complete in about 30 hours.

To remove any dye in excess of that forming a monomolecular dye layer on the particles, the particles are next washed to remove all but an adsorbed dye layer to give a substantially colorless zinc oxide product having adsorbed thereon a monomolecular layer of the sensitizing dye. For washing, a non-polar washing fluid suitably having a dielectric constant of less than about 3 at 20° C. may be used. Suitable materials of this type are solvents such as aliphatic, aromatic, and cycloaliphatic hydrocarbons, for example, hexane, heptane, octane, benzene, toluene, xylenes, cyclopentane, cyclohexane, etc. However, it is preferable to use as a wash fluid a polar material like that used in applying the dye to the oxide particles, providing care is taken that no more dye is removed than that in excess of the amount required to form a monomolecular layer on the particles.

A suitable washing procedure comprises removing the solution in which the dye is applied by filtration, and then washing the zinc oxide particles in the filter with the washing fluid. In such a process, it is desirable to continue washing the dyed particles with washing fluid until the wash fluid is clear. To prevent fixation of excess dye on the sensitized particles and to obviate any cracking of the filter cake which would interfere with good washing, it is desirable always to keep a layer of liquid over the surface of the dyed particles being washed. Generally, amounts of washing fluid of about 80-100 cc. are sufficient to remove excess dye from a 70 gram sample of sensitized zinc oxide, but more or less may be used to get a clear filtrate.

It is believed that the removal of excess dye in this manner is effected by a physical displacement of the treating solution containing excess dye. Dye in excess of that adsorbed on the zinc oxide particles to produce a substantially monomolecular layer is removed in the process.

After excess dye solution has been removed from the particles by washing until the wash fluid is clear, the particles are thoroughly dried, such as by air drying at room temperature, preferably in a dust free atmosphere, or by moderate heating.

An electrostatic printing medium can be prepared from the novel dye sensitized zinc oxide particles above described by applying to a suitable backing material a coating comprising the sensitized photoconductive particles in combination with an electrically-insulating, light-transmissive, transparent or translucent film-forming vehicle or binder, usually resinous. For example, such coatings may contain between about 1 part by weight of dye sensitized zinc oxide particles to 1 part by weight of resin solids and up to 16 parts by weight of these zinc oxide particles per part of resin solids. Particularly good coatings are produced when the ratio by weight of particles to resin solids is about 5:3.

Suitable resin materials, for example, are the silicone resins now used in the art as binders for the photoconductive particles of an electrostatic printing medium, modified according to the present invention as hereinafter described, but other materials now used in the art can also be employed in the invention after suitable modification according to the present disclosure. In general, the conductivity of the binder should be about 10^{-13} mhos/cm. or less.

Electrostatic printing media are prepared by intimately mixing the resin and a solvent therefor with the sensitized zinc oxide particles and then coating a suitable base with the resulting mixture. The thickness of the coating on the base may range from between about 0.5 mil up to 4 mils in thickness, as known in the art. The coatings may be applied by techniques standard in the

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art, such as blade coating or flow coating. Suitable base materials having a smooth surface and moisture and temperature stable electrical properties are known in the art, e.g. aluminum foil or various conductive papers.

Using zinc oxide particles sensitized with one of the dyes disclosed as suitable for sensitization, orthochromatic printing media photoconductive in the presence of light from any predetermined light source can be prepared. Such papers will all be suitable for the reproduction of black and white images, and of monochromatic images corresponding to the orthochromatic sensitivity of the medium.

To achieve optimum sensitivity of a printing medium to visible light of several different wavelengths, or sensitive to light throughout substantially the entire visible spectrum, a plurality of portions of zinc oxide particles, each portion sensitized with a different dye, can be combined. Alternatively, a single batch of zinc oxide particles can be contacted with a plurality of different dyes, either simultaneously or successively. Panchromatic media prepared with pigments sensitized as described above can be used for the monochromatic reproduction of polychromatic images such as color transparencies, for example.

In preparing media sensitive to a broad spectrum, it is preferred to combine a plurality of zinc oxide batches each contacted with a different dye and optimally sensitive in different, preferably overlapping, portions of the visible spectrum. The different batches may be combined in any relative proportions, but it is convenient to combine them in about equal parts by weight. By working with zinc oxide batches sensitized each with a different dye, maximum control of the sensitizing process, minimum interference of the dyes with each other, and maximum photoresponse are achieved.

However, an alternative method yielding sensitized material somewhat less sensitive than that described above can be made by contacting a single batch of zinc oxide with a single solution of a plurality of dyes. In preparing the solutions, adsorption curves of the dyes individually on zinc oxide are used to determine the concentration of each dye required in the mixed solution to give the desired proportion of dyes after adsorption.

Finally, a single batch of zinc oxide can be successively contacted with different dye solutions, with a removal of dye in excess of that required to form a monomolecular layer before contact with the next dye solution. Since it involves many steps, this method is least easy to control.

A better understanding of the invention and of its many advantages can be had by referring to the following specific examples, given by way of illustration.

Example 1a

A dye-sensitized zinc oxide was prepared by forming a paste comprising 70 grams of Florence Green Seal 8 zinc oxide having an average particle diameter of about 3 microns with 100 cc. of a 10^{-5} M solution of Rose Bengal in methanol. The mixture was allowed to stand for about 24 hours at room temperature, with occasional agitation to ensure thorough dispersion.

The mixture was then filtered under vacuum in a Buchner funnel until nearly all of the dye solution had been removed. About 10 cc. of a mixture of equal parts by volume of the dye solution and of toluene were then added to the zinc oxide paste in the filter. Without permitting the paste to become dry, about 100 cc. of toluene were gradually added to the filter, keeping the zinc oxide moist. The amount of toluene washing fluid used was sufficient in amount that the filtrate obtained was clear in color.

After all the washing fluid had passed through the filter, the vacuum was maintained for about 5 to 10 minutes to dry the zinc oxide cake thoroughly.

By comparing spectrophotometric transmission measurements of the original dye-sensitizing solution with measurements made on the filtrate to determine the amount

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of dye present in solution before and after the sensitizing solution had been contacted with the zinc oxide, it was determined that approximately 10^{-4} mols of dye had been adsorbed per gram of zinc oxide.

Using techniques similar to that described above, sensitized zinc oxide particles were prepared using methanol solutions of Eosin Y, acetone solutions of Methylene Blue and Acridine Orange, ethanol solutions of Kryptocyanine, and solutions of Malachite Green and Crystal Violet.

Example 1b

A dye-sensitized zinc oxide was prepared by forming a paste comprising 70 grams of Florence Green Seal 8 zinc oxide having an average particle diameter of about 3 microns with 100 cc. of a 10^{-5} M solution of Rose Bengal in methanol. The mixture was allowed to stand for about 24 hours at room temperature, with occasional agitation to ensure thorough dispersion.

The mixture was then filtered under vacuum in a Buchner funnel until all of the dye solution had been removed. It was then removed from the funnel and mixed with methanol so as to make a slurry. This slurry was then filtered as before. The process of mixing a slurry from the cake and filtering this slurry was repeated until the filtrate obtained became colorless. At this point, the vacuum was maintained for about 5 or 10 minutes thoroughly to remove excess liquid from the cake. The cake was then removed from the filter and allowed to dry in air for at least 24 hours prior to further treatment.

Example 2

An electrostatic printing medium was prepared by combining 50 grams of dried sensitized zinc oxide particles produced by the methods shown in Example 1 with 28 grams of a silicone resin and xylene mixture containing 60 percent resin solids by weight, balance xylene, commercially available under the trade name "SR-82." The materials, together with a zinc-cobalt naphthenate hardener in such amount that the weight of zinc and cobalt therein amounted to 0.5 percent of the weight of resin solids employed, were put into a Waring type blender and mixed for 3 to 5 minutes. The resulting mixture was blade coated onto a conductive paper backing and dried.

Using the same amounts of zinc oxide, silicone resin, and hardener given above, a thin mixture suitable for flow coating of a substrate material was prepared by the addition to the ingredients to be blended of 80 grams of toluene. The mixture was blended as above described, and then applied by flow coating to a suitable backing material. For the preparation of low viscosity mixtures of the latter type, thinning fluids compatible with the resin can be added to adjust the mixture to any desired viscosity. The amounts of such thinning fluid added are not critical, since the fluids are later removed by volatilization. In practice, up to about 150 grams of a thinning fluid can be suitably employed, for example, with the amounts of resin described above.

Example 3

Proceeding as in Example 1a or 1b, a number of batches of zinc oxide particles sensitized with different dyes were mixed in the following proportions:

1339 gms. ZnO sensitized in a 10^{-5} M solution of Rose Bengal;

338 gms. ZnO sensitized in a 10^{-4} M solution of Rose Bengal;

1768 gms. ZnO sensitized in a 10^{-5} M solution of Methylene Blue;

1430 gms. ZnO sensitized in a 10^{-5} M solution of Eosin Y; and

78 gms. ZnO sensitized in a 10^{-4} M solution of Eosin Y.

The resulting mixture was light gray in color and had good sensitivity. When used in preparing a printing medium, as in Example 2 above, the mixture showed

panchromatic response better than commercial papers sensitized with Rose Bengal.

Example 3b

Proceeding as in Example 1b (employing an alcohol wash for the dyed particles), a number of batches of zinc oxide particles sensitized with different dyes were prepared using the following dye solutions:

- Rose Bengal (10^{-5} M);
- Eosin Y (10^{-5} M);
- Methylene Blue (5×10^{-4} M).

Mixtures of the individually dyed ZnO batches with the 60% silicone resin-xylene combination of Example 2, using a 5:3 ratio by weight of ZnO to binder, were then prepared. 42.3 gms. of the mixture containing ZnO sensitized with Methylene Blue were combined with 15.8 gms. of Rose Bengal sensitized ZnO and 16.0 gms. of Eosin Y sensitized ZnO, diluted with 21 ml. of toluene, and applied to a suitable backing to prepare a panchromatic printing medium.

Example 4

A zinc oxide sample was dye sensitized in the manner of Example 1 by contacting with a solution of the following dyes in the concentration indicated. The relative adsorbed concentration of the dyes on the particles, as estimated from adsorption curves is also noted:

Dye	Solution Concentration	Relative Adsorbed Concentration
Crystal Violet.....	$4.5(10^{-4})$ M	1
Methylene Blue.....	$1.95(10^{-3})$ M	1.57
Rose Bengal.....	$2.65(10^{-4})$ M	0.96
Acridine Orange.....	$7.7(10^{-4})$ M	1.82
Eosin Y.....	$6.3(10^{-4})$ M	2.64
Malachite Green.....	$2.0(10^{-4})$ M	0.87

The material so prepared was less photosensitive than the mixture described in Example 2.

Although specific embodiments have been herein shown and described, it is to be understood that they are illustrative and are not to be construed as limiting on the scope and spirit of the invention.

What is claimed is:

1. A method for improving the photoconductive response of zinc oxide particles by dye-sensitization without substantial coloration of the sensitized particles, said particles being adaptable to admixture with a liquid binder for the preparation of coated photosensitive printing media, which process comprises contacting zinc oxide particles, prior to admixture with a binder, with at least one solution, in a solvent having a dielectric constant greater than about 5 measured at 20° C., of at least one adsorbable dye extending the spectral response of said zinc oxide particles into the visible spectrum and selected from the group consisting of acridine, thiazine, phthalein, cyanine, and triphenylmethane dyes, the concentration of said dye in said solution being between about 10^{-2} M and about 10^{-5} M, maintaining said particles in contact

with said solution for at least 3 hours at a temperature below about 200° C., and then washing said particles with a washing fluid having a dielectric constant greater than about 5 measured at 20° C. to remove dye in excess of that forming a substantially monomolecular layer of dye molecules adsorbed on said particles.

2. A method as in claim 1 wherein said solution contains a plurality of dyes.

3. A method as in claim 1 wherein zinc oxide particles are successively contacted with a plurality of dilute dye solutions, and wherein said particles are washed after contact with each solution.

4. A method as in claim 1 wherein zinc oxide particles are contacted with said solution at a temperature above room temperature and below a temperature causing deterioration of the dye.

5. A method for improving the photoconductive response of a mixture of zinc oxide particles by dye sensitization without substantial coloration of the sensitized particles, said particles being adaptable to admixture with a liquid binder for preparation of coated photosensitive printing media, which process comprises contacting each individual batch of a plurality of batches of zinc oxide particles, prior to admixture with a binder, with a different one of a plurality of solutions each containing a different adsorbable dye extending the spectral response of said zinc oxide particles into the visible spectrum, said dye being selected from the group consisting of acridine, thiazine, phthalein, cyanine, and triphenylmethane dyes, the solvent in said solutions having a dielectric constant greater than about 5 measured at 20° C. and the concentration of dye in said solutions being between about 10^{-2} M and about 10^{-5} M, maintaining each batch of particles in contact with its respective dye solution for at least 3 hours at a temperature below about 200° C., and then washing each batch of particles with a washing fluid having a dielectric constant greater than about 5 measured at 20° C. to remove dye in excess of that forming a substantially monomolecular layer of dye molecules adsorbed on said particles, and then combining the separately sensitized batches to form a substantially homogeneous mixture.

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