United States Patent Office 3,241,959 Patented Mar. 22, 1966

3,241,959
SENSITIZED ELECTROPHOTOGRAPHIC COMPOSITION

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No Drawing. Filed July 29, 1963, Ser. No. 298,394
3 Claims. (Cl. 96—1)

This application is a continuation-in-part of our co-pending application Serial No. 53,689, filed September 2, 1960, now U.S. Patent No. 3,128,179 which is a continuation-in-part of our application Serial No. 630,463, filed December 26, 1956 (now abandoned).

This invention relates to improved photoconductive compositions and electrophotographic elements prepared therewith which are useful in making photographic copies, and more particularly, to materials of this kind which are sensitive to ultraviolet and visible light and which have a white to off-white spectral appearance.

It is known that zinc oxide can be employed in making electrophotographic recording elements, for example, by coating a suitable backing member, such as paper with a thin layer of a photoconductive composition comprising finely-divided zinc oxide intimately dispersed in an electrically insulating, film-forming vehicle which has a high dielectric constant and a high dielectric strength so that it will hold an electrostatic charge on its surface in darkness, for example, a silicone resin. Such element when subjected to a blanket high voltage corona discharge on the coated side in the dark, acquires a negative electrostatic charge on the coated surface and is sensitive to light. The element can then be exposed by any of the conventional photographic processes, for example, by projecting a light image on the charged surface whereby the electrostatic charge is lost or reduced in the exposed areas thereof and retained in the masked areas to form a latent electrostatic image charge thereon. This latent image can then be rendered visible, i.e., developed, in any suitable manner, for example, by applying to the exposed surface a developer powder, such as a pigmented resin carrying a positive electrostatic charge. The developer resin is thus attracted to and adheres to the latent image areas of the element. The pigmented image can then be firmly affixed to the photoconductive layer by simply melting and fusing the resin image thereto. Various other means of developing the latent image in the photoconductive layer to a visible image have also been described in the prior art.

One disadvantage of such prior art photoconductive layers containing zinc oxide is that the light-sensitivity of the charged photoconductive layer normally is at its greatest in the ultraviolet region of the spectrum, whereas the exposing source may have its maximum output in a region of the spectrum which lies within the visible region such as an ordinary tungsten lamp. While various means have been previously suggested for sensitizing the zinc oxide so that it has panchromatic or orthochromatic sensitivity, for example, by means of organic dyes such as fluorescein, eosin, rose bengal, crystal violet, malachite green, acridine orange, and the like, these dye methods have not proven particularly satisfactory in commercial practice, since the disadvantage of the strong dyeing of the photoconductive layer in such sensitizations more than offsets the increase obtained in sensitivity. That is, it is very desirable to have some means of sensitizing the photoconductive layer to visible light which does not at the same time permanently color the layer. An element of such characteristics would be especially desirable for use as the final copy of the photographic image. Also, such element would be particularly useful for making color prints of the original subject.

We have now found that zinc oxide photoconductive layers having a white to off-white spectral appearance and panchromatic sensitivity, i.e., having sensitivity in both the ultraviolet and visible regions of the spectrum, can be prepared by incorporating with the zinc oxide composition a plurality of spectral sensitizers principally organic dyes, in such predetermined proportions and quantity as to produce photoconductive layers of the above specified characteristics.

It is, accordingly, an object of the invention to provide an improved white to off-white electrophotographic element which is sensitive to visible light and which can be used as the final copy of photographic images reproduced therewith in accordance with the invention. Another object is to provide a photosensitive composition for producing white to off-white photoconductive recording elements having a spectral sensitivity in the visible range of the spectrum without materially affecting the spectral reflecting characteristics or appearance of the base photoconductive material therein. Another object is to improve the aesthetic quality of the photoconductive compositions and articles coated therewith and at the same time enhance the spectral sensitivity thereof. Another object is to provide an improved method for producing substantially white electrophotoconductive recording elements having a spectral sensitivity in the visible range of the spectrum.

Still another object of the invention is to provide an improved method of producing a zinc oxide-containing photosensitive composition which is of increased sensitivity to visible light and yet which is white to off-white in spectral appearance. Still another object is to provide a white zinc oxide-containing composition which, when coated on a suitable support material and charged with an electrostatic charge is highly sensitive to visible light of colors beyond the blue region of the spectrum so that the charge on the coating imparted by the corona discharge is rapidly and efficiently discharged when subjected to such visible light. Other objects will become apparent hereinafter.

In accordance with the invention, we prepare our improved photoconductive compositions and elements in any convenient manner. For example, by intimately dispersing finely-divided zinc oxide in an organic solvent of a suitable electrically-insulating, film-forming material of high dielectric constant and dielectric strength, and adding the combination of sensitizing dyes thereto in solution form, for example, dissolved in a lower alkanol, such as methanol. However, the dyes making up the combination can also be added individually in any order, or in mixtures of two or more, to the zinc oxide dispersion. Another method that can be used to advantage is to add each dye to a separate zinc oxide dispersion and then mix the separate dye-containing dispersions. Nonpolar organic solvents have been found to be the most suitable for the above zinc oxide dispersions in that any residual solvent does not ordinarily have any deleterious effect on the keeping qualities of the photoconductive layers prepared with such dispersions. Suitable solvents of this kind include the aromatic hydrocarbons such as benzene, toluene and the xylenes. After thorough mixing, the sensitized dispersions can be coated on a suitable support material and dried in the usual manner to give the improved elements of the invention.

Alternatively, the dispersion of zinc oxide in the organic solution of the film-forming material, but without any sensitizing dyes, can be coated on the support material, and, after removal of the organic solvent, can be immersed in a solution blend of the sensitizing dyes, and

then dried. This method has been found useful for some specific applications.

Mixtures of two or more of the film-forming vehicles or binders can be used and plasticizers or similar modifying agents may be incorporated therewith provided such additives do not adversely effect the electrical properties of the photoconductive compositions and layers. The proportion of powdered zinc oxide to film-forming vehicle in the final composition or coating can vary over a wide range, but preferably from 50–90% by weight of the zinc oxide and from 50–10% by weight of the film-forming vehicle. The optimum proportions are based on the nature of the photoconductor, the film-forming vehicle, the dyes, and the results desired. Suitable high dielectric strength film-forming vehicles or binders for the photoconductive zinc oxide compositions may comprise any of the polymeric materials which are commercially available such as styrene-butadiene copolymers, styrene-alkyd resins, silicone-alkyd resins, soya-alkyd resins, polyvinyl esters such as polyvinyl acetate, polyvinyl butyrate, etc., polyvinyl chloride, phenolformaldehyde resins, cellulose derivatives such as cellulose methyl or ethyl ethers, cellulose acetate, cellulose acetatepropionate, etc., polycarbonates, polyurethanes, polyamides such as nylon, polyalkyl acrylates and methacrylates such as polyethyl acrylate, polymethyl methacrylate, and the like. Other binders include materials such as paraffin, mineral waxes, carnauba wax, beeswax, shellac, etc. The methods of making the above resins have been previously described in the prior art. For example, styrene-alkyd resins can be prepared according to the methods described in United States Patents Nos. 2,258,423, 2,361,019 and 2,453,665. Suitable resins also include many that are commercially available under trade names such as Dow Corning Silicone Resin 840, GE Silicone SR–82, Plaskon ST856, Rezyl 405–18, Pliolite S–7 and Styresol 4440. The above-mentioned binders are generally characterized as having marked hydrophobic properties, i.e., being substantially free of any water-solubilizing groups such as hydroxyl, free acid groups or amide groups, and being good electrical insulators or as having high electrical resistivity. These binders can be easily dissolved in organic solvents having a boiling point below the charring temperature of the paper support. Also, these binders have the desirable property of readily dispersing the zinc oxide. It will be understood that some binders are relatively poor insulators and do not provide photoconductive layers which can be stored for prolonged periods of time, after the coated photoconductive layers have been negatively charged. This is particularly noticeable at relatively high humidities and the coated photoconductive layers should be charged shortly before use in such instances. Such problems are well understood in the art.

The zinc oxide employed should generally consist of relatively small particles of less than 0.5 micron mean diameter. Such zinc oxide is readily available and can be purchased under a variety of trade names, such as White Seal No. 7 or Protox No. 168 (New Jersey Zinc Company).

Any mixture of sensitizing dyes can be used in the invention which (1) reflects a gray to black color, (2) which is compatible with the photoconductive zinc oxide, and (3) which produces a white to off-white photoconductor composition or a composition which when coated on the support material and dried has a white to off-white spectral appearance. The best results are obtained when the sensitized zinc oxide layer contains preferably about 0.1 to 1.0 grams of zinc oxide per square foot of surface and preferably from about 0.001 to 0.5% by weight of each optical sensitizing dye, based on the weight of zinc oxide present. Typical dyes that can be used to advantage to prepare dye mixtures of the above characteristics include cyanine (including merocyanine and styryl) dyes such as:

3,3'-diethyl-4,5,4',5'-dibenzothiacyanine chloride
3-carboxymethyl-1'-ethylthia-2'-cyanine iodide
3,3'-diethyl-9-methylthiacarbocyanine bromide
Anhydro-3,3'-di-β-carboxyethyl-5,5'-dichloro-9-ethylthiacarbocyanine hydroxide
Anhydro-3-β-carboxyethyl-5,5'-dichloro-9-ethyl-3'-β-sulfoethylthiacarbocyanine hydroxide
3,3'-di-β-hydroxyethylthiadicarbocyanine bromide
Anhydro-3,3'-di-β-carboxyethylthiadicarbocyanine hydroxide
3-ethyl-5-[di(3-ethyl-2-benzothiazolylidene)isopropylidene]-rhodanine
3-carboxymethyl-5-(3-ethyl-2-(3)-benzothiazolylidene)-rhodanine
3-carboxymethyl-2-(3,3-dicyanoallylidene)benzothiazoline
3-β-carboxyethyl-2-(3,3-dicyanoallylidene)benzothiazoline
2-p-diethylaminostyryl-3-ethylbenzothiazolium iodide

Mixtures of the above dyes will generally include a yellow colored dye, a magenta colored dye and a cyan colored dye.

The methods for making the above and similar dyes have been described in the literature. Among the patents describing the preparation of such dyes are the following: U.S. 1,845,404, 1,934,657, 1,934,659, 1,950,876, 1,969,444, 1,994,563, 2,072,908, 2,107,379, 2,213,238, 2,213,995, 2,231,658, 2,233,509, 2,494,032, 2,503,776, 2,526,632; British 450,958, 606,141, 654,683, 740,770, 751,318.

The support material for the preparation of the electrophotographic recording elements of the invention may be either a relatively insulating material such as paper, or it may be a relatively conducting material such as metal foil or sheet, or paper impregnated with carbon black.

The charged photoconductive elements of the invention prepared as above described can be exposed to a photographic image in the usual manner, and the resulting latent electrophotographic image can then be developed to a visible image in a variety of ways, including those which have been previously employed in electrophotographic processes, such as xerography. A particularly useful means of development is the well known magnetic brush technique which makes use of a mixture comprising a ferromagnetic powder and a pigmented resin powder of particle size from 0.1 to 25 microns and carrying a positive electrostatic charge, deposited on a magnet. This magnetic brush is simply placed in contact with the exposed photoconductive layer and as the brush passes across the negative electrostatic image the positively charged resin particles are attracted to and held by the negatively charged image. The resin powder image can then be fixed by heating to a temperature above the melting point of the resin, but below the charring temperature of the photoconductive element. Accordingly, a low melting point resin is advantageous in the above process. Since the ability of the pigmented resin to accept a positive charge is dependent primarily upon the type of resin selected, it will be apparent that a wide variety of pigments can be used. The pigment merely serves to impart color to the resin and probably imparts very little, if any, influence on the overall charge of the pigmented resin.

The following examples will serve to illustrate further the photoconductive compositions and electrophotographic recording elements of the invention and the manner of their use.

Example 1

Three separate zinc oxide dope compositions were made as follows:

(1) Dispersion A was made by mixing the following ingredients in a mechanical blendor for 30 minutes:

1125.0 g. zinc oxide
750.0 g. Pliolite S–7 resin (70:30 styrene-butadiene copolymer)
1125.0 g. toluene

To 400 grams of above Dispersion A there was added 0.03 g. of the yellow dye, 3-carboxymethyl-2-(3,3-dicyanoallylidene)benzothiazoline, dissolved in about 2 ml. of methanol and one drop of triethylamine. The dispersion was then milled for 5 more minutes.

(2) To 400 grams of above Dispersion A there was added 0.015 g. of the cyan dye, 3,3′-di-β-hydroxyethylthiadicarbocyanine bromide, dissolved in about 2 ml. of methanol and one drop of triethylamine. The dispersion was then milled for 5 more minutes.

(3) This dispersion was made by mixing the following ingredients in a mechanical blendor for about 30 minutes:

150.0 g. zinc oxide
100.0 g. Pliolite S–7 resin (70:30 styrene-butadiene copolymer)
150.0 g. toluene
0.012 g. magenta dye, anhydro-3,3′-di-β-carboxyethyl-5,5′-dichloro-9-ethylthiacarbocyanine hydroxide

The above three dye-containing dispersions were then mixed to make a pan-sensitized zinc oxide dispersion as follows:

25.6 g. of Dispersion 1
74.4 g. of Dispersion 2
74.0 g. of Dispersion 3

This pan-sensitized dispersion gave an equal absorption at the dye peaks in the blue, red and green, respectively, spectral regions to yield a neutral or gray mixture. The mixture was then diluted with toluene to a spraying viscosity of 10 percent solids and sprayed on top of a white unsensitized zinc oxide 70:30 styrene-butadiene paper coating, at an average coverage of 2.14 grams per square foot, to give an off-white coating which was essentially equivalent in color and performance to a layer which had no unsensitized zinc oxide resin undercoat.

Instead of putting each dye in a separate zinc oxide dispersion and mixing the differentially-sensitized dispersions together as above, the dyes can first be dissolved together in methanol in the indicated concentrations to give a solution which appears black to reflected light, and the solution can then be added to the proper amount of zinc oxide dispersion. The resulting xerographic material would also be pan-sensitized, highly reflectant and white to off-white photoconductive paper.

The photoconductive element prepared as above described was (1) charged negatively under a corona charger on the coated side in the dark, (2) exposed to a tungsten light of 3000° K. color through a step tablet having a density increment of 0.1, (3) developed with a magnetic brush using a developer composition comprising three percent finely-divided toner by weight and an iron filing carrier, and (4) fusion of the developed resin image with heat to give a permanent positive image.

The toner composition in the above process consisted of:

200 g. polystyrene
12 g. carbon black
12 g. Spirit Nigrosine (Solvent Black No. 5, Color Index 50415)
8 g. Iosol Black (Solvent Black No. 13)

Example 2

This example illustrates adding a solution of the mixed dyes to the zinc oxide dispersion.

Dispersion B was made by mixing the following ingredients in a mechanical blendor for 15 minutes:

330.0 g. zinc oxide
220.0 g. Pliolite S–7 resin (70:30 styrene-butadiene copolymer)
330.0 g. toluene

To 400 grams of above Dispersion B there was added the following dye mixture, which appeared black to reflected light:

0.0025 g. anhydro-3,3′-di-β-carboxyethyl-5,5′-dichloro-9-ethylthiacarbocyanine hydroxide
0.0081 g. 3-carboxymethyl-5-(3-ethyl-2(3)-benzothiazolylidene)rhodanine
0.0027 g. 3,3′-di-β-hydroxyethylthiadicarbocyanine bromide
16.5 g. methanol

The above dye-containing dispersion was coated on a baryta-coated paper support to a wet thickness of 0.006 inch and the coating was dried. This coating had an off-white appearance. The coating was then charged in the dark, exposed, developed and heat-treated as in Example 1 to yield a permanent xerographic image.

Example 3

The optical sensitizing dyes used in our invention can also be employed in the manufacture of natural three-color photographic images. This process is as follows:

A panchromatically-sensitized electrophotographic paper of the type described in the above example was negatively charged under a corona discharge, exposed by projection through a positive color transparency and a blue filter to a known daylight quality light source for a definite time at a given distance and then developed by the magnetic brush technique described above using iron filings and a yellow pigmented resin, such as Hansa Yellow G pigment, dispersed in Pliolite S–5D. The yellow image corresponding to green, red and black areas of the positive transparency was then transferred electrostatically to the surface of an unsensitized paper receiving sheet and fixed by fusion to the paper surface by heat. Using the same electrophotosensitive paper, after lightly brushing or blowing with air to remove any remaining developer, the same procedure described above was repeated using a green filter and a magenta developer, such as Roberts process red pigment dispersed in Pliolite S–5D. The magenta image corresponding to the blue, red, and black areas of the positive transparency was transferred electrostatically in register to the surface of the same unsensitized receiving sheet containing the yellow image. The magenta image was then fixed by means of heat. Again, the procedure was repeated using a red filter and a cyan developer, such as peacock blue pigment dispersed in Pliolite S–5D. The resulting cyan image corresponding to the blue, green and black areas of the positive transparency was electrostatically transfered in register to the unsensitized receiving sheet containing the yellow and magenta images and fixed by means of heat. The resulting print containing the fused yellow, magenta and cyan transferred images represented a natural three-color reproduction of the positive transparency. Alternatively, instead of fixing each transferred image by heat fusion, the transferred images can be fixed by spraying with a clear resin which hardens upon evaporation of the resin solvent. Also, the above procedure can be modified by using separate sheets of electrophotographic paper which have been optically sensitized to correspond to the spectral transmission range for the three-color separation filters mentioned above.

In a typical process run, a panchromatically-sensitized electrophotographic paper of the type described above containing a mixture of 3-β-carboxyethyl-2-(3,3-dicyanoallylidene)benzothiazoline, anhydro-3,3′-carboxyethyl-5,5′-dichloro-9-ethylthiacarbocyanine hydroxide and 3,3′-di-β-hydroxyethylthiadicarbocyanine bromide as blue, green and red optical sensitizers, respectively, was exposed by projection through a positive Kodachrome transparency and a Wratten No. 47 filter (i.e., a filter transmitting light only between about 370 and 515 mμ) for forty seconds. The above dyes were used in such proportions that a methanol solution of this mixture was gray and the above

paper coated surface containing these dyes in this proportion was white to off-white in spectral appearance. The exposed paper was developed by the magnetic brush technique described above and "developed" with a yellow pigmented resin of the type mentioned above. The yellow image was then transferred to a white clay-coated paper and fixed by fusion to the paper surface via means of heat. Using the same piece of electrophotosensitive paper, after lightly blowing with air to remove any remaining developer, the same procedure described above was repeated using an exposure time of forty seconds, a Wratten No. 61 filter (i.e., a filter transmitting light only between about 475 and 605 mμ) and a magenta pigmented resin of the type described above. The magenta image was then transferred in register to the surface of the receiving sheet and fixed by means of heat. Again, the same procedure was repeated using a Wratten No. 29 filter (i.e., a filter transmitting only light beyond 600 mμ) with an exposure time of four and one-half seconds and with development by means of a cyan pigmented resin. Finally, the cyan image was transferred electrostatically in register to the receiving sheet and fixed by means of heat. The resulting print was a three-color reproduction of the original Kodachrome transparency. The above example was repeated, except that the pigmented resin was not anchored to the paper surface by heat fusion, but by spraying with Krylon (an acrylic spray manufactured by Krylon, Incorporated, Philadelphia, Pennsylvania) after each transfer step. The Pliolite S–5D used above as a vehicle for the developing pigment is a styrene-butadiene copolymer and was chosen because of its frangibility, its positive position relative to iron in a triboelectric series and its ability to become fused to paper at a temperature below 160° C. (the scorch temperature of paper). This resin was milled in a one-quart mill with flint pebbles for 24 hours and then sieved to remove all particles coarser than 200 mesh. The resin was then combined with the desired pigment and ground with mortar and pestle for 10 minutes. To minimize the background in non-transfer processes (as contrasted with the electrostatic transfer mentioned above) it is necessary to fuse the pigment and resin together, crush the mixture, and regrind. To obtain very finely-divided toners, the mixture can be passed through a micronizer of the type described in Haloid U.S. Patent No. 2,659,670, issued November 17, 1953.

It has been found that in some instances, the sensitizing action of certain of the dyes useful in our invention can be improved by heating the sensitized printing papers for a short period of time prior to charging and exposure. A short period of heat treatment appears to increase the efficiency by which the sensitizing dye is able to transfer energy to the photoconductive zinc oxide.

By substituting for the dyes in the above examples, other of the mentioned optical sensitizing dyes, in appropriate amounts, generally similar photoconductive zinc oxide compositions and electrophotographic elements can be prepared. These also can be effectively blanket charged in the dark by a high voltage corona discharge, exposed to a projected visible light image, developed with a magnetic brush and the visible image subjected to heat treatment to give a fused permanent image. They can also be used in making color reproductions.

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

What we claim is:

1. A white to off-white photoconductive composition consisting essentially of finely-divided zinc oxide suspended in an electrically insulating film-forming vehicle and having incorporated therein a substantially gray to black dye blend consisting of a methanol solution of 3 - carboxymethyl - 2-(3,3-dicyanoallylidene) benzothiazoline, 3,3' - di - β-hydroxyethylthiadicarbocyanine bromide and anhydro - 3,3'-di-β-carboxyethyl-5,5'-dichloro-9-ethylthiacarbocyanine hydroxide, said blend being in an amount sufficient to broaden the basic spectral response of said zinc oxide and to produce in combination with said zinc oxide and vehicle an overall spectral reflection imparting to the composition a white to off-white spectral appearance.

2. A white to off-white photoconductive composition consisting essentially of finely-divided zinc oxide suspended in an electrically insulating film-forming vehicle and having incorporated therein a substantially gray to black dye blend consisting of a methanol solution of anhydro - 3,3' - di-β-carboxyethyl-5,5'-dichloro-9-ethylthiacarbocyanine hydroxide, 3 - carboxymethyl - 5 - (3 - ethyl-2(3) - benzothiazolylidene) rhodanine and 3,3' - di - β-hydroxyethylthiadicarbocyanine bromide, said blend being in an amount sufficient to broaden the basic spectral response of said zinc oxide and to produce in combination with said zinc oxide and vehicle an overall spectral reflection imparting to the composition a white to off-white spectral appearance.

3. A white to off-white photoconductive composition consisting essentially of finely-divided zinc oxide suspended in an electrically insulating film-forming vehicle and having incorporated therein a substantially gray to black dye blend consisting of a methanol solution of 3-β-carboxyethyl - 2(3,3 - dicyanoallylidene) benzothiazoline, anhydro - 3,3' - carboxyethyl-5,5'-dichloro-9-ethylthiacarbocyanine hydroxide and 3,3' - di - β-hydroxyethylthiadicarbocyanine bromide, said blend being in an amount sufficient to broaden the basic spectral response of said zinc oxide and to produce in combination with said zinc oxide an overall spectral reflection imparting to the composition a white to off-white spectral appearance.

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