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ZINC OXIDE XEROGRAPHIC LAYERS FOR BIREFLEX COPYING

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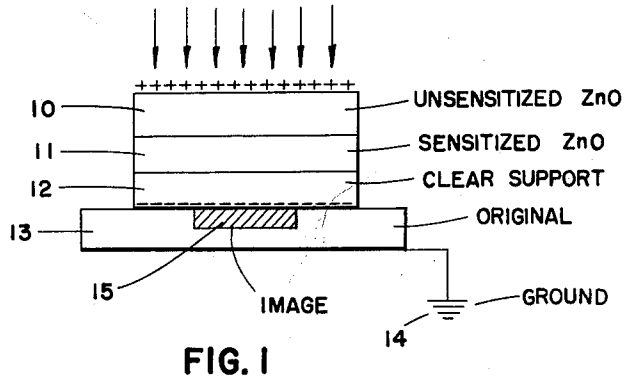


FIG. 1

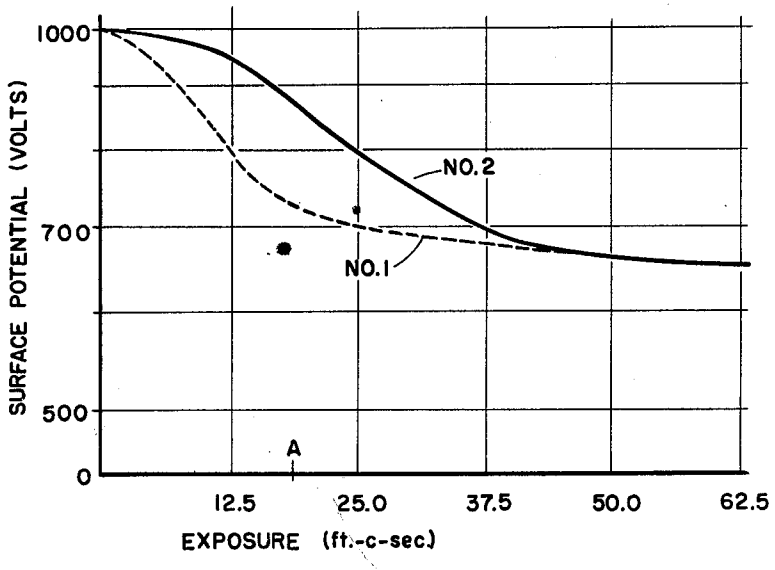


FIG. 2

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ZINC OXIDE XEROGRAPHIC LAYERS FOR BIREFLEX COPYING

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This invention relates to xerography, and more particularly to a xerographic element useful for obtaining a right-reading image directly without having to transfer the image to a receiving sheet. More particularly my invention uses a xerographic process which employs a copying material having a transparent support, making it possible to use a bireflex exposure as shown in the accompanying drawing.

In prior art xerographic processes a photoconductive material, such as zinc oxide, is dispersed in an insulating binder and coated on an electrically conducting support, such as paper, metal foil, and the like. The resulting photographic element, comprising such a conductive support and photoconductive layer, can then be made ready for use by applying a uniform charge to the surface of the photoconductive layer, e.g., by means of a corona discharge. This charge is retained owing to the insulating properties of the layer in the dark. Upon imagewise exposure of the charged photoconductive layer to a light pattern, the charge leaks away in the exposed areas at a rate roughly proportional to the intensity of light falling upon that area of the surface of the photoconductive layer. The latent electrostatic image formed on the surface of the photoconductive layer can then be developed, for example, by dusting with an electrically attractable pigmented powder so that optical density is produced in the non-exposed areas of the layer. By selecting a powder which has as one of its constituents a low-melting solid, e.g., synthetic resin powder, the resulting visible image can be fixed by melting the resin.

Reflex copying is a simple scheme for obtaining an unmagnified duplicate of an original without the use of an optical system for projecting the original on to the photosensitive material. However, in most reflex systems the image on the photosensitive material is laterally transposed, i.e., wrong-reading. The image must therefore be transferred to a second (receiving) sheet to give a right-reading copy of the original. A bireflex copying system is one in which the photosensitive material and the processing sequence are such that a right-reading image of the original is obtained directly on the photosensitive material with the exposure given in the reflex manner. Transferring the image from the photosensitive material to a receiving sheet is unnecessary, and the reflex copying process is considerably simplified.

According to the present invention, right-reading images are directly obtained with the use of a xerographic element comprising a thin, transparent electrically insulating support having coated thereon at least two contiguous, continuous discrete layers comprising photoconductive zinc oxide particles dispersed in a resinous insulating binder, said layers having different optical sensitivities.

Reflex and bireflex copying require that the exposure be given through the photosensitive layer. Since zinc oxide layers are optically highly scattering, differences in intensity due to differences in the reflectance on the original are available only at the bottom surface of the zinc oxide stratum. It is this intensity difference which must be employed to yield an imagewise distribution of surface potential at the positively charged top surface, resulting from the motion of photo-injected charge carriers optically generated in the sensitized layer. The photosensitive region must, therefore, be confined to the surface of the zinc oxide layer near the original. Thus, the optically sensitized layer is coated so that it will be nearest to the original and it is made as thin as possible. The thicker unsensitized top layer is necessary to obtain high developed densities as will be explained hereinafter.

Since only the photoelectrons can move in zinc oxide layers, large changes in surface potential will result only when the electric field in the layer is such as to move the photoelectrons from the sensitized layer where they are generated, through the unsensitized layer, and then to the charged surface. This means that the zinc oxide layer must be charged positively. When coated on a conducting support, zinc oxide layers store only negative charges. However, if the support is an insulator, positive charges can always be stored and elements for bireflex copying are readily obtained. The preferred supports are transparent insulators, such as acetate or polyethylene terephthalate (Mylar) sheeting, or other plastic type supports of the type commonly employed in silver halide photography.

The support must be transparent to the radiation to which the sensitized layer is responsive in my process in order that the radiation can reach the surface of the original where the differences in reflectance on the original can control the exposure of the sensitized layer. Because many originals are diffuse reflectors, it is necessary that the support be thin in order to provide sharp copied images. A transparent insulating sheeting of one-fourth mil thickness, e.g., one-fourth mil polyethylene terephthalate, is an excellent support, although thicker films (e.g., 3 mils) can be used with some sacrifice in image quality.

The change in surface potential is determined not only by the number of carriers that move, but also by the distance which they move, i.e., the change in capacitance resulting from such movement. To get a large change in capacitance, the carriers must move a relatively large distance, thus the top layer is relatively thick with respect to the bottom layer (usually at least twice as thick), thereby giving a large change in capacity.

Cascade, or cascade-like, development with an electrically insulating carrier minimizes the background density that can accompany the development of images on insulator-supported xerographic layers.

In preparing a multilayer xerographic material of the present invention comprising at least two separate continuous and contiguous layers having substantially different spectral sensitivities, the following condition for such a material must be fulfilled:

(1) The layer must be capable of being independently exposed, e.g., by being sensitive to radiation of different wavelengths.

The present invention will be further understood by reference to the accompanying drawings in which

FIG. 1 is a diagrammatic cross-section of a xerographic element in accordance with the present invention and

FIG. 2 illustrates the change in surface potential of a multilayer bireflex structure as a function of exposure.

Referring to FIG. 1, photoconductive layers **10** (unsensitized) and **11** (panchromatic) of zinc oxide in a suitable organic binder are coated on a thin, transparent, insulating support **12**. The multilayer configuration is such that **10** contains no spectral sensitizer and **11** is panchromatically sensitized. The xerographic element is placed on the document to be copied, **13** having a ground **14**, and a positive surface charge applied on the surface of **10** by conventional charging techniques, e.g., corona discharge. The assembly is then exposed to radiation which is absorbed only by the layer **11** and the character being copied, **15**. The result of the exposure is to decrease the surface potential in the regions above

the highly reflecting areas of the original more than in the region above the absorbing characters of the original. This pattern of varying surface potential is then developed by a cascade method with a negatively charged toner which will deposit preferentially in the regions of higher surface potential thereby giving a right-reading copy of the original, i.e., a bireflex copy.

In FIG. 2 are typical data of the change in surface potential of a multilayer bireflex structure as a function of exposure. Curve 1 holds when a multilayer assembly is exposed while in contact with a white sheet of paper, while curve 2 was obtained when the same layer was backed by a black sheet of paper. The best exposing condition is that at which the greatest potential difference between the two curves is obtained, i.e., point A. If ultraviolet radiation reaches and is absorbed by the top layer, there is no difference between curves 1 and 2 and no reflex copying is observed in this particular system, since zinc oxide has high sensitivity to such radiation.

In preparing the xerographic materials of the present invention, one approach is to prepare a coating composition comprising a solution of the insulating resinous binder containing a dispersion of photoconductor, e.g., zinc oxide, cadmium sufide, zinc sulfide, etc. Different photoconductors can be used in the respective layers, and depending upon their spectral absorption characteristics, mixtures of photoconductors can also be used. Organic photoconductors, such as polyvinylcarbazole, can also be used, though usually less advantageously. Where a spectral sensitizing dye is to be incorporated, the dye can either be added directly to the composition, or it can be dissolved separately in a suitable solvent and added to the composition before coating. The resulting dope can then be coated on a suitable support in a well-known manner, such as spray coating, roller coating, doctor-blade coating, etc. The layer is then allowed to dry before any subsequent layers are applied. Normally, drying of each layer is done before a second layer is applied, although where suitable viscosities are maintained, additional layers can be added before drying is complete.

The resinous component of the photoconductive layers of the elements of the invention includes a large number of polymers having fairly high dielectric strength and which are good electrically insulating, film-forming vehicles. These materials include resins sold under trade names, such as Plaskon ST 856, Rezyl 405–18, Pliolite S–7, Styresol 4440, DC-804, SR–82, etc. These resins comprise styrene-butadiene copolymers, silicone resins, styrene-alkyd resins, silicone-alkyd resins, soya-alkyd resins, polyvinyl chloride, polyvinyl acetate, etc., and mixtures of such binders. The methods of making such resins have been previously described in the prior art, for example, styrene-alkyd resins can be prepared according to the method described in U.S. Patent 2,361,019, October 24, 1944; U.S. Patent 2,258,423, October 7, 1941; and U.S. Patent 2,453,665, November 9, 1948. Other binders, such as paraffin, mineral waxes, etc., can also be employed. These binders are generally characterized as having marked hydrophobic properties, that is, are substantially free of water-solubilizing groups such as hydroxyl, free acid groups, amide groups, etc., and as being good electrical insulators or having high electrical resistivity. These binders can be easily dissolved in organic solvents having a boiling point below the softening temperature of the transparent plastic support. These binders also have the desirable property of readily dispersing the particulate photoconductors. Some resinous binders will be found to be not as good insulators as desired, and therefore, electrostatically charged layers containing such binders cannot be stored for a long a period of time as when prepared with other binders of the more desirable type.

There are instances also in which it may be desirable to use a different resinous binder for the separate layers of a particular xerographic material. For example, since styrene-butadiene copolymers possess properties which give an improved humidity resistance and toughness, it may be desirable to use a copolymer of this type as the vehicle for the surface layer.

Zinc oxide, which is the preferred photoconductive constituent of the xerographic members of the invention should have a relatively small particle size on the order of less than 0.5 micron mean diameter. Suitable photoconductive zinc oxides are readily obtainable and can be purchased under a variety of trade names, such as White Seal, No. 7 or Green Seal, No. 8 (New Jersey Zinc Company) either of which are so-called "French process" zinc oxides. When preparing the photoconducting layers of the present invention, sufficient resinous binder can advantageously be employed with the photoconductive zinc oxide so that each of the zinc oxide particles is covered and isolated from the surrounding particles in the composition. The most useful or optimum ratio of photoconductive material to binder for a particular binder can be readily determined by making a series of test coatings wherein the quantity and relative amounts of photoconductive material to binder are employed. If desired, zinc oxide prepared by the methods of U.S. Patents 2,727,807 and 2,727,808, issued December 20, 1955, may be used in the elements of the invention. It has been found that different types of zinc oxide can be used advantageously in the respective strata of electrophotographic materials. For example, the conventional white type of zinc oxide can be employed in the surface layer, and the "pink type" (U.S. Patents 2,727,807 and 2,727,808) having inherent sensitivity extended to the longer wavelengths, e.g., green and red regions of the spectrum, can be employed in an element as shown in FIG. 1 of the accompanying drawing.

Spectral sensitizing dyes which are useful in sensitizing the bottom layer according to the present invention can comprise any of the dyes which give spectral sensitization in the desired visible region of the spectrum. Suitable green-light sensitizing dyes, for example, comprise:

A. Merocyanine dyes:

(1) 3-β-carboxyethyl-2-(3,3-dicyanoallylidene) benzothiazoline
(2) 3-carboxymethyl-2-(3,3-dicyanoallylidene) benzothiazoline
(3) 3-carboxymethyl-5-[(3-methyl-2-(3H)-thiazolinylidene)isopropylidene]rhodanine
(4) 3-ethyl-5-[3-carboxymethyl-3(3H)-benzoxazolylidene)ethylidene]-rhodanine
(5) 5-[3-ethyl-2-(3H)-benzoxazolylidene) ethylidene]-3-β-sulfoethyl-2-thio-2,4(3,5)-oxazoledione
(6) 3-carboxymethyl-5-[(3-ethyl-2(3H)-benzothiazolylidene)-ethylidene]rhodanine
(7) 4-[(3-ethyl-2(3H)-benzothiazolylidene) isopropylidene]-3-methyl-1-(p-sulfophenyl)-5-pyrazolone
(8) 3-(2,5-disulfophenyl)-5-[(3-ethyl-2(3H)-benzothiazolylidene)-ethylidene]rhodanine

B. Cyanine dyes:

(9) 3,3'-diethyl-4,5,4',5'-dibenzothiacyanine chloride
(10) 3-β-carboxyethyl-1'-ethyl-6'-methoxy-5-phenylthia-2'-cyanine iodide
(11) 3,3'-diethyl-4,5,4',5'-dibenzoxacyanine iodide
(12) 3,3'-diethylthiazolinocarbocyanine iodide
(13) 3,3'-diethyloracarbocyanine iodide
(14) 3,3'-diethyl-9-methyloxaselenacarbocyanine iodide

Typical dyes for conferring sensitivity in the red region of the spectrum are:

A. Dicarbocyanine dyes:

(15) 3,3'-di-β-hydroxyethylthiadicarbocyanine bromide

(16) Anhydro-3,3'-di-β-carboxyethylthiadicarbocyanine hydroxide

(17) 3,3'-diethyloxathiadicarbocyanine iodide

(18) 3,3'-diethyl-4,5,4',5'-dibenzothiadicarbocyanine iodide

(19) 3'-carboxymethyl-3-ethyloxathiadicarbocyanine iolide

(20) 3-carboxymethyl-3'-ethyloxathiadicarbocyanine iodide

(21) 3,3'-di(carboxymethyl)oxathiadicarbocyanine bromide

B. Carbocyanine dyes:

(22) 3,3'-diethyl-9-methyl-4,5,4',5'-dibenzothiacarbocyanine chloride

(23) Anhydro-3,3'-di-β-carboxyethyl-5,5'-dichloro-9-ethyl thiacarbocyanine hydroxide

(24) Anhydro-3-β-carboxyethyl-5,5'-dichloro-9-ethyl-3'-β-sulfoethylthiacarbocyanine hydroxide

(25) 9-ethyl-3,3'-di-β-hydroxyethylthiacarbocyanine iodide

C. Complex merocyanine dyes:

(26) 2-(3-carboxymethyl-4-oxo-2-thiono-5-thiazolidylidene)-3-ethyl-5-[3-ethyl-2(3H)-benzoxazolylidene)ethylidene]-4-thiazolidone

(27) 3-ethyl-5-[(1-ethyl-4(1H)-quinolylidene) ethylidene]-2-(3-ethyl-4-oxo-2-thiono-4-thiazolidylidene)-4-thiazolidone

(28) 2-(3-carboxymethyl-4-oxo-2-thiono-5-thiazolidylidene)-3-ethyl-5-[(3-ethyl-2(3H)-benzothiazolylidene)-α-ethyl-ethylidene]-4-thiazolidone

(29) 5-[(1-ethyl-3(1H)-β-naphthothiazolylidene)-α-phenylethylidene]-3-β-methoxyethyl-2(3-β-methoxyethyl-4-oxo-2-thiono-5-thiazolidylidene)-4-thiazolidone

(30) 5-[(1-ethyl-2(1H)-β-naphthothiazolylidene)-α-ethyl-ethylidene]-3-β-methoxymethyl-2-(3-β-methoxyethyl-4-oxo-2-thiono-5-thiazolidylidene)-4-thiazolidone

Blue sensitizing dyes, such as those described in Jones and Stewart U.S. application Serial No. 805,157, filed April 9, 1959, can also be used.

The present invention is further illustrated by the following examples, in which all parts are by weight unless otherwise specified.

Example 1

A two-layer xerographic material, in which the outer or surface layer was unsensitized and the inner or under layer was sensitized, was prepared on a ¼ mil polyethylene terephthalate support as follows:

A 0.3 mil layer comprising 80 parts of powdered French process zinc oxide, 20 parts of a binder comprising 90% SSA–42 (a styrene-alkyd resin sold by Schenectady Varnish Co.) and 10% of a high styrene content styrene-butadiene copolymer (sold under the trade name Pliolite S–7 by the Goodyear Rubber and Tire Co.) which had been cross-linked with a rare earth naphthanate, and 10^{-7} mole of Rose Bengal (tetraiododichloro-fluorescein, Na salt) was coated on the support and covered with a 0.8 mil layer of 50 parts of a binder, comprising 80 parts of a styrene-butadiene copolymer (Pliolite S–7) and 20 parts of Silicone SR–82 (a silicone resin purchased from the General Electric Company) and 50 parts of powdered French process zinc oxide.

The above xerographic element was exposed to a line negative using tungsten illumination filtered with a Wratten No. 8 Filter, i.e., a filter transmitting substantially only radiation beyond about 470 mμ, the xerographic element being placed in contact with the original as illustrated in FIG. 1 of the accompanying drawing. The exposed element was then "developed" by treatment with an electroscopic powder of the type illustrated in Walkup Canadian Patent 495,360, issued August 18, 1953, using the conventional cascade development technique (see British Patent 693,905, published July 8, 1953, showing a device suitable for this operation). The electroscopic powder adhered only to the parts of the element retaining the greatest positive charge, being held roughly in proportion to the potential of the charge. Substantially no powder adhered to the less charged portions of the element giving an accurate copy of the original.

Instead of using an electroscopic powder of the type described in Canadian 495,360, other electroscopic powders or toners having a negative charge thereon can be employed. The preparation of such powders is well known to those skilled in the art and is the subject of a number of patents, such as Canadian 550,574, issued December 24, 1957, Canadian 557,577, issued May 20, 1958, Canadian 564,712, issued October 14, 1958, etc. The triboelectric effect required to produce an appropriate electroscopic powder is discussed in Canadian 495,360, and it is to be understood that any of the conventional negatively charged electroscopic powders can be employed in my novel process. For example, an electroscopic powder which is described in Canadian Patent 495,360 comprises a mixture of 20 parts Amberol F–71, a phenol-formaldehyde resin manufactured by Resinous Products & Chemical Co., 222 West Washington Square, Philadelphia 5, Pennsylvania, and 1 part carbon black such as Raven Bead Carbon Black manufactured by Binney & Smith Co., 41 East 42nd Street, New York 7, New York. The electrostatic powder is prepared by mixing the above ingredients and breaking them to a 16-mesh size or smaller, after which approximately 225 grams of the mixture are placed in a one-half gallon capacity ball mill jar containing an aluminum scraper. The jar is filled to approximately three-quarters its capacity with ½" diameter balls and the mixture ball milled for about four hours, after which it is removed from the ball mill jar and fused on a hot plate under suitable heating lamps or by other suitable means. The mixture is then cooled and broken into approximately 16-mesh size particles, following which it is micropulverized to an average size of from 1 to 20 microns. In addition, this invention can be carried out with any of the commercially available xerographic developers having a negatively charged toner, such as Xerox Copyflo P–1, Xerox 914, Xerox Long-life #10, Hunt Grafofax #5 (using a glass bead carrier), etc.

In general, it will be recognized that improved rendition is obtained where electroscopic powders of very small particle size are employed. Particle sizes larger than about 7 to 8 microns tend to produce a somewhat fuzzy image. Electroscopic powders having an average particle size of 5 microns produce quite pleasing copies.

Example 2

A second xerographic element was prepared as in Example 1 with the sensitized layer comprising 50 parts zinc oxide and 50 parts of a binder comprising 80 parts of a styrene-butadiene copolymer (Pliolite S–7) and 20 parts of Silicone SR–82 with similar results.

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

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

1. A xerographic element useful for bireflex copying comprising a thin, transparent, electrically insulating support having coated thereon a photoconductive zinc oxide layer spectrally sensitized to the visible region of the

spectrum and coated over said spectrally sensitized zinc oxide layer, a continuous discrete layer of spectrally unsensitized photoconductive zinc oxide, said unsensitized zinc oxide layer being of substantially greater thickness than said optically sensitized layer.

2. A xerographic element as defined in claim 1 wherein said insulating support comprises a hydrophobic linear polyester.

3. A xerographic element as defined in claim 2 wherein said spectrally sensitized zinc oxide layer comprises Rose Bengal.

4. A xerographic method of producing copies of an original by a bireflex copying technique comprising photoexposing to visible actinic radiation a two-ply combination comprising

(*a*) an original bearing an image on one surface and

(*b*) a xerographic element comprising (1) a thin, transparent insulating support having coated thereon (2) at least one photoconductive layer having substantial sensitivity to said visible actinic radiation and coated over said sensitized photoconductive layer (3) at least one discrete photoconductive layer having substantially no sensitivity to said visible actinic radiation,

said support being placed in surface contact with the side of said original bearing an image and said outer photoconductive layer having a positive electrostatic charge, said exposure being made so that said visible actinic radiation passes firstly through said non-sensitive photoconductive layer, then through said sensitized photoconductive layer and said support, so that reflections of said visible actinic radiation from said original cause photoexposure, said exposure being continued until said electrostatic charge has leaked away from said outer layer substantially only where exposure has occurred in said sensitized photoconductive layer, and developing a visible image by applying a negatively charged electroscopic powder to the surface of said outer layer.

5. A xerographic method of producing copies of an original by a bireflex copying technique comprising photoexposing to visible actinic radiation a two-ply combination comprising

(*a*) an original bearing an image on one surface and

(*b*) a xerographic element comprising (1) a thin, transparent insulating support having coated therein (2) at least one spectrally sensitized photoconductive zinc oxide layer having substantial sensitivity to said visible actinic radiation and coated over said spectrally sensitized photoconductive zinc oxide layer (3) at least one discrete non-spectrally sensitized photoconductive zinc oxide layer having substantially no sensitivity to said visible actinic radiation,

said support being placed in surface contact with the side of said original bearing an image and said non-spectrally sensitized, outer, photoconductive zinc oxide layer having a positive electrostatic charge, said exposure being made so that said actinic radiation passes firstly through said non-spectrally sensitized zinc oxide layer, then through said spectrally sensitized photoconductive zinc oxide layer and said support, so that reflections of said visible actinic radiation from said original cause photoexposure to occur in said spectrally sensitized zinc oxide layer, said exposure being continued until said electrostatic charge has leaked away from said outer, non-spectrally sensitized zinc oxide layer only where exposure has occurred in said spectrally sensitized zinc oxide layer, and developing a visible image by applying a negatively charged electroscopic powder to the surface of said outer non-spectrally sensitized zinc oxide layer.

6. A method according to claim 5 wherein said non-spectrally sensitized layer is at least twice as thick as said spectrally sensitized zinc oxide layer.

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