ELECTROPHORETIC IMAGING PROCESS USING 8,13-DIOXIDONAPHTHA-2,1-b:2',3'-d)-FURAN-6-CARBOXAMIDE PIGMENTS

Lester Weinberger, Rochester, N.Y., assignor to Xerox Corporation, Rochester, N.Y., a corporation of New York

Filed Dec. 28, 1964, Ser. No. 421,377
Int. Cl. B41M 5/20; C23b 13/00; G03g 7/00
U.S. Cl. 204—181

19 Claims

ABSTRACT OF THE DISCLOSURE

N - substituted - 8,13-dioxidonaphtho (2,1-b; 2',3'-d)-furan-6-carboxamides as electrically photosensitive pigments useful in photoelectrographic imaging, in xerographic plates and in deformation imaging.

This invention relates in general to imaging methods, more specifically, the invention concerns the use of electrically photosensitive pigments in electrophotographic imaging systems.

There has been recently developed an electrophoretic imaging system capable of producing color images which utilize conductive pigment particles. This process is described in detail and claimed in copending applications Ser. Nos. 384,737 now U.S. 3,844,565; 384,681, now abandoned and 384,680 now abandoned, all filed July 23, 1964. In such an imaging system, various colored light absorbent particles are suspended in a non-conductive liquid carrier. The suspension is placed in contact with an electrically charged substrate, subjected to a potential difference and exposed to an image. As these steps are completed, the conductive pigment migration takes place in configuration, providing a visible image at one or both of the electrodes. An essential component of the system is the suspended particles which must be intensely colored pigments which are electrically photosensitive and which apparently undergo a net change in charge polarity upon exposure to activating radiation, through interaction with one of the electrodes. The images are produced in color because mixtures of two or more differently colored pigments which are each sensitive only to light of a specific wavelength or narrow range of wavelengths are used. Pigments used in this system must have both intense pure colors and be highly photosensitive. The pigments of the prior art often lack the purity and brilliance of color, the high degree of photosensitivity, and/or the preferred correlation between the peak spectral response and peak photosensitivity necessary for use in such a system.

Another imaging system which utilizes electrically photosensitive material is the xerographic process as described in U.S. Patent 2,897,691 to C. F. Carlson. Here, the photosensitive material must be an effective conductive insulating paper, i.e., must be capable of holding an electrostatic charge in the dark and dissipating the charge to a conductive substrate when exposed to light. In the fundamental process, a base sheet of relatively low electrical resistance such as metal, paper, etc., having a conductive insulating coating thereon, is electrostatically charged in the dark. The charged coating is then exposed to a light image. The charges leak off rapidly to the base sheet in proportion to the intensity of light to which the particular area is exposed, the charge being substantially retained in non-exposed areas, forming an electrostatic latent image. After exposure, the coating is contacted with electrostatic marking particles in the dark. These particles adhere to the areas where the electrostatic charge remains, forming a powder image corresponding to the electrostatic latent image. Where the base sheet is relatively inexpensive, such as paper, the image may be fixed directly to the plate, as by heat or solvent fusing. Alternatively, the powder image may be transferred to a sheet of transfer material, such as paper, and fixed thereon.

Many photosensitive materials useful in the xerographic process are known in the art, e.g., vitreous selenium, sulfur, anthracene, zinc oxide, polyvinyl chromic and several of these different materials are in commercial use today, each has deficiencies in such areas as photographic speed, spectral response, durability, reusability and cost such that there is a continuing need for improved materials.

A third class of electrophotographic imaging which utilizes electrically photosensitive materials has recently been developed. This class consists of two systems of surface deformation imaging which are generally referred to as "frost" imaging and "relief" imaging. Frost imaging is described in detail in a publication entitled "A Cyclic Xerographic Method Based on Frost Defomation" by R. W. Gundlach and C. J. Claus, Journal of Photographic Science and Engineering, January-February edition, 1963. Relief imaging is described in detail in U.S. Patents 3,055,006; 3,163,872 and 3,113,179.

For use in frost imaging, for example, a plate may be made by overcoating a conductive substrate with a layer of a photosensitive insulating material, which is then overcoated with a thermoplastic material. Alternatively, the photosensitive material may be dispersed in particulate form in the thermoplastic layer and the mixture coated directly onto the conductive substrate. Typically, a uniform electrostatic charge is imposed on the plate surface, then the plate is exposed to a light and shadow image to be reproduced. The charge is dissipated in light-streaked areas but remains in unexposed areas. The plate is heated or treated with a solvent vapor until the electrostatic attraction forces of the charge pattern exceed the surface tension forces of the film. When this threshold condition is reached, a series of very small air pockets or wrinkles are formed on the film surface, the depth of the wrinkles in any particular area of the film being dependent upon the intensity of charge in that area. This gives the image a frosted appearance. Other methods of frost and relief charging, exposing, and developing are described in the above mentioned publication and patents.

Many of the presently known conductive materials have an excessively limited spectral response and low photographic speed and, thus, are incapable of producing optimum frost or relief images.

It is, therefore, an object of this invention to provide novel electrophotographic imaging processes which overcome the above noted deficiencies.

It is another object of this invention to provide novel electrophoretic imaging processes.

It is another object of this invention to provide novel xerographic imaging-electrostatic processes.

It is still another object of this invention to provide novel surface deformation imaging processes.

It is still another object of this invention to provide novel electrophoretic imaging systems capable of reproducing color images.

It is still another object of this invention to provide novel frost imaging processes.

It is still another object of this invention to provide novel relief imaging processes.

It is still another object of this invention to provide novel xerographic plates having maximum spectral and photosensitive responses in ranges other than those of prior plates.

The foregoing objects and others are accomplished in accordance with this invention fundamentally, by provid-
ing novel electrophotographic imaging processes utilizing compositions having the general formula:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{N} & \quad \text{H} \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R_2 - R_3 \) are each selected from the group consisting of \( \text{H, CH}_3, \text{C}_2\text{H}_5, \text{NO}_2, \text{OCH}_3, \text{OC}_2\text{H}_5, \text{CN, SO}_2\text{NH}, \text{SO}_2\text{NHCH}_3, \text{COH, Cl, F, Br, I} \). The compositions of the general formula given above belong to the class of 8,13-dioxinaphtho(2,1-b; 2',3'-d)-furan-6-carbox-anilides. These compositions may be made by reacting 2,3-dichloro-1,4-naphthoquinone with any suitable anilide. Typical anilides are: 2-hydroxy-3-naphthol-4'-methylanilide; 2-hydroxy-3-naphthol-4'-methoxyanilide; 2-hydroxy-3-naphthol-2'-nitroanilide and 2-hydroxy-3-naphthol-3'-carboxyaminolide. Suitable anilides include those having the general formula:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{N} & \quad \text{H} \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R_2 - R_3 \) are each selected from the group consisting of \( \text{H, CH}_3, \text{C}_2\text{H}_5, \text{NO}_2, \text{OCH}_3, \text{OC}_2\text{H}_5, \text{CN, SO}_2\text{NH}, \text{SO}_2\text{NHCH}_3, \text{COCH}_3, \text{CO}_2\text{H}, \text{SO}_2\text{NHCH}_3 \text{Cl, F, Br, I} \). The compositions produced by the above reaction have the common characteristics of a brilliant, intense yellow color; of insolvability in water and the common organic solvents, e.g., benzene, toluene, acetone, carbon tetrachloride, chloroform, and aliphatic hydrocarbons; and of unusually high photosensitive response. Of the compositions within the general formula listed above, those having a single substituent in the "para" position, e.g., 8,13-dioxinaphtho(2,1-b; 2',3'-d)-furan-6-carbox-p-methoxy-anilide, and mixtures thereof are preferred for use in electrophotographic imaging processes since they are most simply and economically synthesized, have especially pure color and are most highly photosensitive. Of these, the optimum substituent has been found to be the methoxy group. This has been found to give the most desirable combination of color and photosensitivity. Since the shade or tone of the compositions and the spectral and photosensitive responses vary slightly depending upon the substituent used, intermediate values of these variables may be obtained by mixing several of the different compositions. The compositions within the general formula listed above, and mixtures thereof, are especially useful as photosensitive pigment particles in electrophoretic imaging processes. An exemplary electrophoretic imaging system is shown in the figure.

Referring now to the figure, there is seen a transparent electrode generally designated 1 which, in this exemplary instance, is made up of a layer of optically transparent glass 2 overcoated with a thin optically transparent layer 3 of tin oxide, commercially available under the name NESA glass. This electrode will hereafter be referred to as the "injecting electrode." Coated on the surface of injecting electrode 1 is a thin layer 4 of finely divided photosensitive particles dispersed in an insulating liquid carrier. The term "photosensitive," for the purposes of this application, refers to the properties of a particle which, once attracted to the injecting electrode, will migrate away from it under the influence of an applied electric field when it is exposed to certain electromagnetic radia-

For a detailed theoretical explanation of the apparent mechanism of operation of the invention, see the above mentioned copending applications Ser. Nos. 384,737; 384,361 and 384,680, the disclosures of which are incorporated herein by reference. Liquid suspension 4 may also contain a sensitizer and/or a binder for the pigment particles which is at least partially soluble in the suspending or carrier liquid as will be explained in greater detail below. Adjacent to the liquid suspension 4 is a second electrode 5, hereinafter called the "blocking electrode," which is connected to one side of the potential source 6 through a switch 7. The opposite side of potential source 6 is connected to the injecting electrode 1 so that when switch 7 is closed, an electric field is applied across the liquid suspension 4 between electrodes 1 and 5. An image projector made up of a light source 8, a transparency 9, and a lens 10 is provided to expose the dispersion 4 to a light image of the original transparency 9 to be reproduced. Electrode 5 is made in the form of a roller having a conductive central core 11 connected to the potential source 6. The core is covered with a layer Baryta paper. The pigment suspension is exposed to the image to be reproduced while a potential is applied across the blocking and injecting electrodes between the roller 5 and switch 7. Roller 5 is caused to roll across the top surface of injecting electrode 1 with switch 7 closed during the period of image exposure. This light exposure causes exposed pigment particles originally attracted to electrode 1 to migrate through the liquid and adhere to the surface of the blocking electrode, leaving behind a pigment image on the injecting electrode surface which is a duplicate of the original transparency 9. After exposure, the relatively volatile carrier liquid evaporates off, leaving behind the pigment image. This pigment image may then be fixed in place as, for example, by placing a lamination over its top surface or by virtue of a dissolved binder material in the carrier liquid such as paraffin wax or other suitable binder that comes out of solution as the carrier liquid evaporates. About 3% to 6% by weight of paraffin binder in the carrier has been found to produce good results. The carrier liquid itself may be paraffin wax or other suitable binder. In the alternative, the pigment image remaining on the injecting electrode may be transferred to another surface and fixed thereon. As explained in greater detail below, this system can produce either monochrome or polychromatic images depending upon the type and number of pigments suspended in the carrier liquid and the color of light to which this suspension is exposed in the process.

Any suitable insulating liquid may be used as the carrier for the pigment particles in the system. Typical carrier liquids are deionized, deodacene, N-tetradecane, paraffin, beeswax or other thermoplastic materials, Solio Odorless Solvent 3440, (a kerosene fraction) and Isopar-G (a long chain saturated aliphatic hydrocarbon). Good quality images have been produced with voltages ranging from 300 to 5,000 volts in the apparatus of the figure.

In a monochromatic system, particles of a single composition are dispersed in the carrier liquid and exposed to a black-and-white image. A single color image results, corresponding to conventional black-and-white photography. In a polychromatic system, the particles are selected so that those of different colors respond to different wave lengths in the visible spectrum corresponding to their principal absorption bands. Also, the pigments should be selected so that their spectral response curves do not have substantial overlap, thus allowing for color separation and subtractive multicolor image formation. In a typical multicolor system, the particle dispersion should include cyan colored particles sensitive mainly to red light, magenta particles sensitive mainly to green light and yellow colored particles sensitive mainly to blue light. When mixed together in a carrier liquid, these particles produce a black appearing liquid. When one or more of the particles are caused to migrate from base electrode 11 toward an upper
electrode, they leave behind particles which produce a color equivalent to the color of the impinging light. Thus, for example, red light exposure causes the cyan colored pigment to migrate, leaving behind the magenta and yellow pigments which combine to produce red in the final image. In the same manner, blue and green colors are reproduced by red and yellow and magenta, respectively. When white light impinges upon the mix, all pigments migrate, leaving behind the color of the white or transparent substrate. No exposure leaves behind all pigments which combine to produce a black image. This is an ideal technique of subtractive color imaging in that the particles are not only each composed of a single color, but, in addition, they perform the dual functions of final image colorant and photosensitive medium.

It has been found that the compounds of the general formula given above are surprisingly effective when used in either a single or multicolor electrophoretic imaging system. Their good spectral response and high photosensitivity result in dense, brilliant images. It is known that in general cyan and magenta pigment particles separate from the trimix more easily and form more dense images than do the usual yellow pigments. The yellow pigments herein disclosed, however, have surprisingly good color separation and image density characteristics.

Any suitable different colored photosensitive pigment particles having the desired spectral responses may be used with the yellow pigments of this invention to form a pigment web on a carrier liquid for color imaging. From about 2 to about 10 percent pigment by weight have been found to produce good results. The addition of small amounts (generally ranging from 0.5 to 5 mol percent) of electron donors or acceptors to the suspensions may impart significant increases in system photosensitivity.

The following examples further specifically define the present invention with respect to the use of the compositions of the general formula given above in electrophoretic imaging processes. Parts and percentages are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of the electrophoretic imaging process of the present invention.

All of the following Examples I-XXII are carried out in an apparatus of the general type illustrated in the figure with the imaging mix 4 coated on a NESA glass substrate through which exposure is made. The NESA glass surface is connected in series with a switch, a potential source, and the conductive center of a roller having a coating of Baryta paper on its surface. The roller is approximately 2 1/4 inches in diameter and is moved across the plate surface at about 1.45 centimeters per second. The plate employed is roughly 3 inches square and is exposed with a light intensity of 8,000 foot candles as measured on the uncoated NESA glass surface. Unless otherwise indicated, 7 percent by weight of the indicated pigments in each example are suspended in Sohio Odorless Solvent 3440 and the magnitude of the applied potential is 2500 volts. All pigments which have a relatively large particle size as received commercially or as made are ground in a ball mill for 48 hours to reduce their size to provide a more stable dispersion which improves the resolution of the final images. The exposure is made with a 3200 K. lamp through a 0.30 neutral density wedge filter to measure the sensitivity of the suspensions to white light and then WRATTEN FILTERS 29, 61 and 47B are individually superimposed over the light source in separate tests to measure the sensitivity of the suspensions to red, green and blue light respectively.

**Example I**

About 7 parts of 8,13-dioxodinaphtho-(2,1-b,2',3'-d)-furan-6-carbox-p-methoxyanilide is suspended in about 100 parts of Sohio Odorless Solvent 3440. The mixture is coated on the NESA glass substrate and a negative potential is imposed on the roller electrode. The plate exposed through a WRATTEN 29 filter and the neutral density step wedge filter, thus exposing the plate to red light. The results are tabulated in the table below.

**Example II**

A test is run as in Example I above, except that a WRATTEN 61 filter is used in place of the WRATTEN 29 filter, thus exposing the plate to green light. The results are tabulated in the table.

**Example III**

A test is run as in Example I above, except that a WRATTEN 47B filter is used in place of the WRATTEN 29 filter, thus exposing the plate to blue light. The results are tabulated in the table.

**Example IV**

A test is run as in Example I above, except that no color filter is used, thus exposing the plate to white light. The results are tabulated in the table.

**Example V**

A test is run as in Example I above, except that the roller potential is positive rather than negative. As in Example I, a WRATTEN 29 filter is used to expose the plate to red light. The results are tabulated in the table.

**Example VI**

A test is run as in Example V above, except that a WRATTEN 61 filter is used in place of the WRATTEN 29 filter, thus exposing the plate to green light. See table for results.

**Example VII**

A test is run as in Example V above, except that a WRATTEN 47B filter is used in place of the WRATTEN 29 filter, thus exposing the plate to blue light. See table for results.

**Example VIII**

A test is run as in Example V above, except that no WRATTEN filter is used, thus exposing the plate to white light. See table for results.

**Example IX**

About 7 parts of 8,13-dioxodinaphtho-(2,1-b; 2',3'-d)-furan-6-carbox-p-methoxyanilide is suspended in about 100 parts Sohio Odorless Solvent 3440. The mixture is tested as in Example I, above. The WRATTEN 29 filter is used to expose the plate to red light. The results are tabulated in the table.

**Example X**

A test is run as in Example IX above, except that a WRATTEN 61 filter is used in place of the WRATTEN 29 filter, thus exposing the plate to green light. See table for results.

**Example XI**

A test is run as in Example IX above, except that a WRATTEN 47B filter is used in place of the WRATTEN 29 filter, thus exposing the plate to blue light. See table for results.

**Example XII**

A test is run as in Example IX above, except that no WRATTEN filter is used, thus exposing the plate to white light. See table for results.

**Example XIII**

A test is run as in Example IX above, except that a positive rather than negative potential is imposed on the roller electrode. The plate is exposed through a WRATTEN 29 filter, thus exposing the plate to red light. See table for results.

**Example XIV**

A test is run as in Example XIII above, except that a WRATTEN 61 filter is used in place of the WRATTEN 29 filter, thus exposing the plate to green light. See table for results.
A test is run as in Example XIII above, except that a Wratten 47f filter is used in place of the Wratten 29 filter, thus exposing the plate to blue light. See table for results.

A test is run as in Example XIII above, except that no Wratten filter is used, thus exposing the image to white light. See table for results.

The electrophoretic sensitivity of the various pigments to red, green, blue and white light is tested according to conventional photographic methods and the results are recorded in the table above. In the table, the first column lists the number of the test example. The second column gives the positive or negative electrical potential applied to the roller electrodes in volts. The Wratten filters used in each example between the light source and the NESA plate are listed in column three. The fourth column lists the color of the light which is permitted to fall on the NESA plate. The fifth column gives the photographic speed of the photosensitive film in foot candles. The photographic speed is the result of a curve of photographic speed plotted against the logarithm of exposure in foot candles; f/1.7 being 0.3 gamma toe speed and f/2.2 being 0.3 gamma shoulder speed. Gamma, as listed in column 6, is a standard photographic term referring to the slope of the above mentioned curve. The maximum and minimum reflection densities produced are listed in columns 7 and 8, respectively. As shown by the above table, the tested yellow pigments are sensitive, in an electrophoretic sense, to blue light only. As can be seen, the pigments are essentially non-responsive to red and green light, having slight, negligible, response to green light. Thus, the response to these pigments to white light is essentially identical to their response to blue light.

In each of Examples XVII—XXII, below, a suspension including equal amounts of three different colored pigments is made up by dispersing the pigments in finely divided form in Solicitud Odorless Solution 3440 so that the pigments constitute about 8% by weight of the mixture. This mixture may be referred to as a "tri-mix." The mixtures are individually tested by coating them on a NESA glass substrate and exposing them as in Example I above, except that a multicolor Kodachrome transparency is interposed between the light source and the plate instead of the neutral density and Wratten filters. Thus, a multicolored image is projected on the plate as the roller moves across the surface of the coated NESA glass substrate. A Baryta paper blocking electrode is employed and the roller is held at a negative potential of about 2500 volts with respect to the substrate. The roller is passed over the substrate six times, being cleaned after each pass. Potential application and exposure are both continued during the entire period of the six passes by the roller. After completion of the six passes, the quality of the image left on the substrate is evaluated as to density and color separation.

The pigments consist of a magenta pigment, Watchung Red B, a barium salt of 1-((4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, C.I. No. 15865; a cyan pigment, Cyan GTFN, the beta form of copper phthalocyanine, C.I. No. 74100 and as a yellow pigment, 8,13-dioxodinaphtho-(2,1-b; 2',3'-d) furan-6-carboxylic acid. This tri-mix is exposed to a multicolor image and produces a full color image of good density and color separation.

The pigments consist of a magenta pigment, Naphtho Red B, 1-(2'-methoxy-5'-nitrophenylazo)-2-hydroxy-3-naphthoic acid, C.I. No. 12355; a cyan pigment, Cyan Blue, 3,3'-methoxy-4,4'-diphenyl-bis-(1'-azo-2'-hydroxy-3'-naphthoic acid), C.I. No. 21180, and as a yellow pigment, 8,13-dioxodinaphtho- (2,1-b; 2',3'-d)- furan-6-carboxylic acid. This trimix is exposed to a multicolor image and produces a full color image of good density and excellent color separation.

The pigments consist of a magenta pigment, Vulcan Fast Red BBE Toner 35-2201, 3,3'-dime- thoxy - 4,4'- diphenyl-bis(1'-phenyl-3'-methyl-4'-azo-2'-paroxylene-5'-one), C.I. No. 21200, available from Callway Colors; a cyan pigment, a polychlor substituted copper phthalocyanine, C.I. No. 74260, and a yellow pigment, 8,13-dioxodinaphtho-(2,1-b; 2',3'-d)- furan-6-carboxylic acid. This trimix is exposed to a multicolor image and produces a full color image of good density and color separation.

The pigment suspension consists of a magenta pigment, Calcium Litho Red, the calcium lake of azo dye, 1-(2'-azoinaphthalene-1'-sulfonic acid)-2-naphthoic acid, C.I. No. 15630; a cyan pigment, Mosolite Fast Blue G.S., the alpha form of metal-free phthalocyanine, C.I. No. 74100, and a yellow pigment, 8,13-dioxodinaphtho-(2,1-b; 2',3'-d)- furan-6-carboxylic acid. This trimix is exposed to a multicolored image and produces a full color image of satisfactory density and good separation.
Example XXII

The pigment suspension consists of a magenta pigment, Indostar Brilliant Scarlet Toner, 3,4,9,10-bis(N,N'-methoxy-phenyl-imido)-p-ylene, C.I. No. 71140; a cyan pigment, Cyan Blue XR, the alpha form of copper phthalocyanine, and as a yellow pigment, 5,13-dioxodinaphtho-(2,1-b; 2',3'-d)-furan-6-carboxy-3'-cyano - 5' - methoxy) anilide. This trimix is exposed to a multicolored image and produces a full color image of good density and color separation.

The compositions of the general formula given above are also useful in xerographic imaging systems. For use in such a process, the plates may be produced by coating a relatively conductive substrate, e.g., aluminum or paper, with a dispersion of particles of the photosensitive pigment of the above general formula in a resin binder. The pigment-resin layer may also be cast as a self-supporting film. The plate formed may be both with or without an overcoating on the photconductive layer. As a third alternative to the above noted self-supporting layer and substrate supported layer, the photo-sensitive pigment-resin photoconductive layer may be used in the formation of multilayer sandwich configurations adjacent a dielectric layer, similar to that shown by Golovin et al., in the U.S. Patent No. 3,298,420 (DuPont) for a New Electrophotographic Process, Effected by Means at Combined Electret Layers, Doklady Akad. Nauk SSSR, vol. 129, No. 5, pp. 1008-1011, November-December 1959.

When it is desired to coat the pigmented resin film on a substrate, various supporting materials may be used. Suitable materials for this purpose include aluminum, steel, brass, metalized or tin oxide coated glass, semi-conductive plastics and resins, paper and other convenient materials. Any suitable dielectric material may be used to overcoat the photoconductive layer. A typical overcoating is bichromated shellac.

Any suitable organic binder or resin may be used in combination with the pigment to prepare the photoconductive layer of this invention. In order to be useful the resin used in the present invention should be more resistive than about 10$^{10}$ and preferably more than 10$^{22}$ ohms per centimeter under the conditions of xerographic use. Typical resins include thermoplastics such as polystyrene, polystyrene-acetate, polystyrene-diene chloroprene, polystyrene-divinylbenzene, polycrylic, polyacrylonitrile, silicone resins, chlorinated rubber, and mixtures and copolymers thereof, where applicable; and thermosetting resins such as epoxy resins including halogenated epoxy resins, novolac resins, phenolic, epoxy-phenolic copolymers, epoxy urea-formaldehyde copolymers, epoxy melamine-formaldehyde copolymers and mixtures thereof, where applicable. Other typical resins are epoxy esters, vinyl epoxy resins, tallow-modified epoxies, and mixtures thereof, where applicable. In addition to the above noted binder materials, any other suitable resin may be used if desired. Also, other binders such as paraffin and mineral waxes may be used if desired.

The pigments may be incorporated in the dissolved or melted binder resin by any suitable means such as strong shear agitation, preferably with simultaneous grinding. These include ball milling, roller milling, sand milling, ultrasonic agitation, high-speed blending and any desirable combination of these methods. Any suitable range of pigment-resin ratios may be used.

A pigment-resin slurry (or the pigment-resin melt) may be applied to the conductive substrate by any of the well known painting or coating methods, including spraying, flow coating, knife coating, electro-coating, Mayer bar downwax, dip coating, reverse foil coating, etc. Spraying in an electric field may be preferred for the smoothest finish and drying for convenience in the laboratory. The setting, drying and/or curing steps for these plates are generally similar to those recommended for films of the particular binder used for other painting applications. For example, pigment-epoxy plates may be cured by adding a cross-linking agent and storing according to approximately the same schedule as other baking enamels made with the same resins and similar pigments for painting applications. A very desirable aspect of these pigments is that they are stable against chemical decomposition at the temperatures normally used for a wide variety of bake-on enamels, and therefore, may be incorporated in very hard glossy photoconductive coatings, similar to automotive or kitchen appliance resin finishes.

The thickness of the photoconductive films may be varied from about 1 to about 100 microns, depending on their required individual purpose. Self-supporting films, for example, cannot usually be manufactured within 10 microns, and they are easiest to handle and use in the 15 to 75 micron range. Coatings, on the other hand, are preferably formed in the 5 to 30 micron range. For certain compositions and purposes, it is desirable to provide an overcoating; this should usually not exceed the thickness of the photoconductive coating, and preferably not above one-quarter of the latter. Any suitable overcoating material may be used, such as bichromated shellac.

The invention as it pertains to xerographic imaging processes will be further described with reference to the following examples, which describe in detail various preferred embodiments of the present invention. Parts, ratios and percentages are by weight unless otherwise stated.

Xerographic plates for use in the following examples are prepared as follows: Mixtures using specific pigments and resin binders are prepared by ball milling the pigment or a solution of a resinous binder and one or more solvents until the pigment is well dispersed. This is done by adding the desired parts of the pigment to the desired parts of resin solution in a suitable mixing vessel. A quantity of one-eighth inch steel balls are added and the vessel is rotated for approximately one half hour in order to obtain a homogeneous dispersion. The cooled slurry is applied onto an aluminum substrate with a wire drawdown rod and force dried in an oven for about 3 minutes at about 100°C. The coated sheets are dark rested for about 1 hour and then tested.

In the following examples, plates are tested as follows. The plate is charged negatively by corona discharge about 400 volts and exposed to a light and shadow image. The plate is cascade developed using Xerox 1824 developer, The powder image produced on the plate corresponds to the projected image. The developed image may be then either fused to the plate or may be electrically transferred to a detail copy sheet and further fused. Where the image is transferred, the plate may then be cleaned of residual toner and may be reused as in the above described process.

Example XXIII

The xerographic plate is prepared by initially mixing about 2 parts of Lucite 2042, an ethylmethacrylate polymer, about 18 parts benzene, and about 1 part of 8,13-dioxodinaphtho - (2,1-b; 2',3'-d) - furan 6 - carboxy - 4' - methoxyanilide (made by the process described above). This mixture is coated onto an aluminum substrate to a thickness of about 8 microns and cured. The plate is then charged, exposed for about 45 seconds to a light and shadow image using a Simonsen Omega D3 enlarger equipped with a tungsten light source operating at 2950 K. The illumination level (illumination meter Model No. 756) is about 20 foot candles as measured with a Westwood Illumination Meter Model No. 756), and developed as above described. The image produced is heat fused directly onto the plate. The image produced, while not optimum, was found to be satisfactory.

Example XXIV

The xerographic plate is prepared by initially mixing a binder and a solvent as in Example XXIII above with about 1 part of 8,13-dioxodinaphtho-(2,1-b; 2',3'-d)-furan-
6-carbox-4'-methyl-anilide (made by the process above described.) This mixture is coated onto an aluminum substrate to a thickness of about 8 microns and cured. The plate is charged, exposed for about 45 seconds to a light and shadow image using a Siemens Omega D3 enlarger equipped with a tungsten light source operating at 2950° K. color temperature (illumination level incident on the plate is 2.8 foot candles as measured with a Weston Illumination Meter Model No. 756), and developed. While a poor image was produced, electrometer testing of a second coating prepared as in this example was found to have measurable, but low xerographic sensitivity.

Example XXV

The xerographic plate is prepared by initially mixing about 3 parts Lucite 2042 with about 100 parts benzene and about 10 parts of 8,13-dioxinadipphtho(2,1-b; 2',3'-d)-furan-6-carbox-4’-methoxyanilide (made by the process above described). This mixture is coated onto an aluminum substrate to a thickness of about 8 microns and cured. The plate is then charged, exposed for about 45 seconds to a light and shadow image using a Siemens Omega D3 enlarger equipped with a tungsten light source operating at 2950° K. color temperature (illumination level incident on the plate is 2.8 foot candles as measured with a Weston Illumination Meter Model No. 756), and developed. The image is heat fused onto the plate surface. A satisfactory, but no optimum, image resulted.

Example XXVI

The xerographic plate is prepared by initially mixing about 10 parts Lucite 2042, with about 90 parts benzene and about 2 parts 8,13-dioxinadipphtho(2,1-b; 2',3'-d)-furan-6-carbox-4’-methoxyanilide (made by the process above described). This mixture is coated onto an aluminum substrate to a thickness of about 10 microns and cured. The plate is then charged, exposed through a film positive for about 30 seconds to a high intensity, long wave, ultra-violet lamp (1680 microwatts/cm² of 3660 A.U. radiation at a distance of 18 inches), and developed. The powder image developed on the plate is electrostatically transferred to a receiving sheet and heat fused. The image on the receiving sheet corresponds to the contact exposed original. The plate is wiped clean of any residual toner and is reused as in the above described manner. The image on the receiving sheet is of excellent quality.

Example XVII

The xerographic plate is prepared by initially mixing about 10 parts Lucite 2042, with about 90 parts benzene and about 2 parts 8,13-dioxinadipphtho(2,1-b; 2',3'-d)-furan-6-carbox-4’-methoxyanilide (made by the process above described). The mixture is coated onto an aluminum substrate to a thickness of about 8 microns and cured. The plate is then charged, contact exposed through a film positive for about 30 seconds to a high intensity, long wave, ultra-violet lamp (1680 microwatts/cm² of 3660 A.U. radiation at a distance of 18 inches), and developed. The image on the receiving sheet is of excellent quality and corresponds to the contact exposed original. The plate is wiped clean of any residual toner and is reused as in the above described manner.

The third xerographic imaging process in which the above listed photosensitive pigments are useful is that referred to as "surface deformation imaging." As discussed above, this includes both frost and relief deformation of the surface of a deformable layer in image configuration. Any suitable imaging method may be used in the surface deformation imaging process of the present invention. The following methods are typical:

(1) The photoconductive thermoplastic layer is first substantially uniformly charged and exposed to a light and shadow image to be reproduced. The material is then heated until it deforms to form a frost pattern corresponding to the light and shadow image. The frost image thus formed is subsequently fixed or set by permitting the heat deformable layer to cool below its melting point. The image may be erased by reheating the layer in a charge free condition to its softening point.

(2) The thermoplastic layer is selectively charged in imagewise configuration. Subsequently, the thermoplastic material is heated, thereby producing a frost image only in those areas upon which the charge was initially deposited. The material is then cooled to fix the image. The image may be erased by reheating if desired.

(3) In an alternative imaging process, the thermoplastic layer is uniformly charged and exposed to a light and shadow image. The material is then exposed to a solvent vapor, which softens the surface so that it deforms to form a frost pattern corresponding to the light and shadow image. Next, the solvent is removed by evaporation to fix or set the image. This image may be layer erased by resoftening the layer surface, by heat or additional solvent vapor.

(4) In still another alternative, a relief image may be formed by scanning the thermoplastic layer with an electron beam, either while the layer is softened, or just prior to heat or solvent softening. This image may be set by returning the layer to its pre-softened condition.

(5) Any of the methods described in detail in copending applications 193,277, now U.S. 3,196,011 and 232,049, now U.S. 3,244,083, filed May 5, 1962 and Oct. 23, 1962 respectively, may be used in the process of this invention. For example, the methods of forming the frost or relief imaging may vary depending upon the intended use of the resulting product. In certain situations, the heat deformable layer may be pre-treated before uniformly charging the surface thereof, in addition, various suitable methods may be used to selectively fix and/or erase the material in imagewise configuration.

Any suitable material may be used as the surface deformable coating over the photoconductive layer or as the binder for the photosensitive pigments in a self-deformable layer. Typical surface deformable thermoplastic polymers are low molecular weight polymers of oligomers. Any suitable polymers may be used in the surface deformation process of this invention; typical polymers are aromatic polymers such as polystyrene, alpha methylstyrene; copolymers made from styrene and other materials such as vinyl toluene, methylstyrene, polyvinyl methyl styrene, chlorinated styrene, and polymers and copolymers made from petroleum cuts and indene polymers; phenolics such as phenol aldehyde resins, phenol formaldehyde resins and mixtures thereof; vinyl polymers such as polyvinylacetate, polyvinylalcohol, polyvinylbutyral, butylmethacrylate-styrene polymers, butylmethacrylate - alkoholylated styrene copolymers, styrene-methacrylatebutadiene terpolymers; organo-poly-siloxanes such as polydimethyl-siloxane; polymers such as acrylic esters, bisphenol-A type polymers; bisphenol-A copolymers; complex hydrocarbon polymers such as hydrogenated polystyrene and mixtures and copolymers thereof. If desired, deformation characteristics of the films may be improved by incorporating on the surface thereof of thin surface skins as disclosed in copending application 338,323 filed Aug. 7, 1964 and now abandoned.

The following examples will further specifically define the heat deformable imaging process of the present invention. Parts and percentages are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of surface deformable imaging according to the present invention. Broadly, the surface deformable image, either "relief" or "frost," may be formed either (1) by direct deformation of the thermoplastic binder containing the photosensitive pigment or (2) by overcoating the pigment-
binder layer with a thermoplastic layer which is itself deformable.

Example XXVIII

A plate is prepared by initially mixing about 2 parts Lucite 2042, an ethyl-methacrylate polymer, about 18 parts benzene, and about 1 part of 8,13-dioxoanaptho-(2,1-b; 2',3'-d) furan-6-carbox-4'-methoxanilide (made by the process above described). This mixture is coated onto a aluminum substrate to a thickness of about 8 microns and cured. The plate is then overcoated with about a 10 micron layer of Picoflex 100-A (a polyvinylchloride resin). The composition plate is then charged negative to about 450 volts in the dark by means of a corona discharge, exposed for about 15 seconds by projection using a Simmons Omega D3 enlarger equipped with an f/4.5 lens and a tungsten light source of 2900 K. color temperature. Illumination level at the exposure plane is about four foot candles as measured with a Weston Illumination Meter Model No. 756. The plate is then developed by placing the plate on a heated platen maintained at about 70°C. As the plate is heated to the softening point of the overcoating, a series of very small wrinkles or folds spontaneously forms in unexposed areas, giving the image a frosted appearance.

Example XXIX

The plate is prepared by initially mixing about 2 parts Lucite 2042, about 18 parts benzene and about 1 part of 8,13-dioxoanaptho-(2,1-b; 2',3'-d) furan-6-carbox-4'-methylnilide (made by the process above described). This mixture is coated onto an aluminum substrate to a thickness of about 8 microns and dried. The plate is then overcoated with about a 10 micron layer of Staybelle ester No. 10. The composite plate is given an electrostatic charge, exposed to a light and shadow image, and heated to the softening point of the overcoating, as in Example XXVI above. When this threshold point is reached, a frost image again appears.

Example XXX

A plate is prepared by initially mixing about 10 parts Lucite 2042, about 90 parts benzene and about 2 parts 8,13-dioxoanaptho-(2,1-b; 2',3'-d) furan-6-carbox-4'-methoxanilide (made by the process above described). This mixture is coated onto an aluminum substrate to a thickness of about 8 microns and cured. The plate is then overcoated with about a 10 micron layer of Picoflex 100-A. The composite plate is then charged to a negative potential of about 400 volts in the dark by means of a corona discharge. The charged plate is exposed through a film positive for about 30 seconds to a high intensity, long wave, ultraviolet lamp (1680 microwatts/cm² of 3600 A.U. radiation at a distance of 18 inches.) The electrostatic latent image on the plate is then developed by placing the composite plate on a heated platen maintained at about 70°C. As the plate is heated to the softening point of the overcoating, a frost image corresponding to the original appears.

Although specific components and proportions have been described in the above examples relating to electrophoretic, xerographic, and heat deformable imaging systems, other suitable materials, as listed above, may be used with similar results. In addition, other materials may be added to the pigment compositions or to the pigment-resin compositions to synergize, enhance or otherwise modify their properties. The pigment compositions and/or the pigment-resin compositions of this invention may be dye sensitized, if desired, or may be mixed or otherwise combined with other photoconductors, both organic and inorganic.

Other modifications and ramifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. The method of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between at least two electrodes, at least one of which is partially transparent, and simultaneously exposing said suspension to an image through said transparent electrode with activating electromagnetic radiation whereby a pigment image made up of particles is formed on at least one of said electrodes; said suspension comprising a plurality of finely divided particles of at least one color, said particles of one color comprising a photosensitive pigment having the general formula:

\[ R_s \]

2. The method of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between at least two electrodes, at least one of which is partially transparent, and simultaneously exposing said suspension to an image through said transparent electrode with activating electromagnetic radiation whereby a pigment image made up of particles is formed on at least one of said electrodes; said suspension comprising a plurality of finely divided particles of at least one color, said particles of one color comprising a photosensitive pigment having the general formula:

\[ R_s \]

3. The method of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between at least two electrodes, at least one of which is partially transparent, and simultaneously exposing said suspension to an image through said transparent electrode with activating electromagnetic radiation whereby a pigment image made up of particles is formed on at least one of said electrodes; said suspension comprising a plurality of finely divided particles of at least one color, said particles of one color comprising a photosensitive pigment having the general formula:

\[ R_s \]

4. The method of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between at least two electrodes, at least one of which is a blocking electrode, and simultaneously exposing said suspension to an image with activating electromagnetic radiation whereby a pigment image made up of particles is formed on at least one of said electrodes; said suspension comprising a plurality of finely divided particles of
3,448,029

at least one color, said particles of one color comprising a photosensitive pigment having the general formula:

$$\text{O}$$

wherein $R_1$—$R_3$ are each selected from the group consisting of $H$, $\text{C}_2\text{H}_5$, $\text{NO}_2$, $\text{OCH}_3$, $\text{CH}_3$, $\text{OC}_2\text{H}_5$, $\text{SO}_2\text{NH}_2$, $\text{CO}_2\text{H}$, $\text{CN}$, $\text{CO}_2\text{C}_2\text{H}_5$, $\text{SO}_2\text{NHC}_2\text{H}_5$, $\text{Cl}$, $\text{Br}$, $\text{F}$, $\text{I}$.

5. The method of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between at least two electrodes, at least one of which is a blocking electrode, and simultaneously exposing said suspension to an image with activating electromagnetic radiation whereby a pigment image made up of particles is formed on at least one of said electrodes; said suspension comprising a plurality of finely divided particles, at least one of said particles comprising $8,13$-dioxodinaphtho-(2,1-b; 2',3'-d)-furan-6-carbox-4'-methoxysanilide.

6. The method of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between two electrodes, at least one of which is at least partly transparent, said suspension comprising a plurality of finely divided particles of at least two different colors in an insulating carrier liquid, the particles of each color comprising a photosensitive pigment whose principle light absorption band substantially coincides with its principal photosensitive response, simultaneously exposing said suspension to a light image through said partially transparent electrode and then separating said electrodes whereby a pigment image is formed on the surface of at least one of said electrodes, the particles of one color comprising compositions having the general formula:

$$\text{O}$$

wherein $R_1$—$R_3$ are each selected from the group consisting of $H$, $\text{C}_2\text{H}_5$, $\text{NO}_2$, $\text{OCH}_3$, $\text{CH}_3$, $\text{OC}_2\text{H}_5$, $\text{SO}_2\text{NH}_2$, $\text{CO}_2\text{H}$, $\text{CN}$, $\text{CO}_2\text{C}_2\text{H}_5$, $\text{SO}_2\text{NHC}_2\text{H}_5$, $\text{Cl}$, $\text{Br}$, $\text{F}$, $\text{I}$.

8. The method of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between two electrodes, at least one of which is at least partly transparent, said suspension comprising a plurality of finely divided particles of at least two different colors in an insulating carrier liquid, the particles of each color comprising a photosensitive pigment whose principle light absorption band substantially coincides with its principal photosensitive response, simultaneously exposing said suspension to a light image through said partially transparent electrode and then separating said electrodes whereby a pigment image is formed on the surface of at least one of said electrodes, the particles of one color comprising compositions having the general formula:

$$\text{O}$$

50

wherein $R_1$—$R_3$ are each selected from the group consisting of $H$, $\text{C}_2\text{H}_5$, $\text{NO}_2$, $\text{OCH}_3$, $\text{CH}_3$, $\text{OC}_2\text{H}_5$, $\text{SO}_2\text{NH}_2$, $\text{CO}_2\text{H}$, $\text{CN}$, $\text{CO}_2\text{C}_2\text{H}_5$, $\text{SO}_2\text{NHC}_2\text{H}_5$, $\text{Cl}$, $\text{Br}$, $\text{F}$, $\text{I}$.

10. The method of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between two electrodes, at least one of which is a blocking electrode, said suspension comprising a plurality of finely divided particles of at least two different colors in an insulating carrier liquid, the particles of each color comprising a photosensitive pigment whose principle light absorption band substantially coincides with its principal photosensitive response, simultaneously exposing said suspension to a light image and then separating said electrodes whereby a pigment image is formed on the surface of at least one of said electrodes, the particles of one color comprising compositions having the general formula:

$$\text{O}$$

75

wherein $R_1$—$R_3$ are each selected from the group consisting of $H$, $\text{C}_2\text{H}_5$, $\text{NO}_2$, $\text{OCH}_3$, $\text{CH}_3$, $\text{OC}_2\text{H}_5$, $\text{SO}_2\text{NH}_2$, $\text{CO}_2\text{H}$, $\text{CN}$, $\text{CO}_2\text{C}_2\text{H}_5$, $\text{SO}_2\text{NHC}_2\text{H}_5$, $\text{Cl}$, $\text{Br}$, $\text{F}$, $\text{I}$.
color comprising compositions having the general formula:

wherein R is selected from the group consisting of C₂H₅, NO₂, OCH₃, CH₃, OC₂H₅, SO₂NH₂, CO₂CH₃, CN, CO₂C₂H₅, SO₂NHC₅H₄, Cl, Br, F, I.

11. The method of electrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between two electrodes, at least one of which is a blocking electrode, said suspension comprising a plurality of finely divided particles of at least two different colors in an insulating carrier liquid, the particles of each color comprising a photosensitive pigment whose principle light absorption band substantially coincides with its principal photosensitive response, simultaneously exposing said suspension to a light image and then separating said electrodes whereby a pigment image is formed on the surface of at least one of said electrodes, the particles of one color comprising 8,13-dioxodimaphtho-(2,1-b; 2',3'-d)-furan-6-carboxy-4'-methoxanilide.

12. A xerographic plate comprising a photoconductive layer comprising a binder material and a composition having the general formula:

wherein R₁-R₅ are each selected from the group consisting of H, C₂H₅, NO₂, OCH₃, CH₃, OC₂H₅, SO₂NH₂, CO₂CH₃, CN, CO₂C₂H₅, SO₂NHC₅H₄, Cl, Br, F, I.

13. A xerographic plate comprising a photoconductive layer comprising a binder material and a composition having the general formula:

wherein R₁-R₅ are each selected from the group consisting of H, C₂H₅, NO₂, OCH₃, CH₃, OC₂H₅, SO₂NH₂, CO₂CH₃, CN, CO₂C₂H₅, SO₂NHC₅H₄, Cl, Br, F, I.

14. A xerographic plate comprising a photoconductive layer comprising a binder material and 8,13-dioxodimaphtho-(2,1-b; 2',3'-d)-furan-6-carboxy-4'-methylanilide.

15. A process for forming a latent xerographic image on a photoconductive layer comprising a photoconductive pigment and an organic binder, which comprises electrostatically charging said layer and exposing said layer to a pattern of activating electromagnetic radiation; said photoconductive pigment comprising the composition having the general formula:

wherein R₁-R₅ are each selected from the group consisting of H, C₂H₅, NO₂, OCH₃, CH₃, OC₂H₅, SO₂NH₂, CO₂CH₃, CN, CO₂C₂H₅, SO₂NHC₅H₄, Cl, Br, F, I.

16. A process for forming a latent xerographic image on a photoconductive layer comprising a photoconductive pigment and an organic binder, which comprises electrostatically charging said layer and exposing said layer to a pattern of activating electromagnetic radiation; said photoconductive pigment comprising the composition having the general formula:

wherein R₁-R₅ are each selected from the group consisting of H, C₂H₅, NO₂, OCH₃, CH₃, OC₂H₅, SO₂NH₂, CO₂CH₃, CN, CO₂C₂H₅, SO₂NHC₅H₄, Cl, Br, F, I.

17. A process for forming a latent xerographic image on a photoconductive layer comprising a photoconductive pigment and an organic binder, which comprises electrostatically charging said layer and exposing said layer to a pattern of activating electromagnetic radiation; said photoconductive pigment comprising the composition having the general formula:

wherein R₁-R₅ are each selected from the group consisting of H, C₂H₅, NO₂, OCH₃, CH₃, OC₂H₅, SO₂NH₂, CO₂CH₃, CN, CO₂C₂H₅, SO₂NHC₅H₄, Cl, Br, F, I.

18. A method for forming an image on a surface deformable recording medium which comprises electrostatically charging a recording medium, exposing said medium to a pattern of light and shadow and maintaining the surface of said medium in a sufficiently viscous condition to thereby deform at least a portion of said surface in a configuration corresponding to said pattern of light and shadow wherein said recording medium comprises photoconductive pigment particles in a thermoplastic binder said photoconductive pigment comprising the composition having the general formula:  

wherein R₁-R₅ are each selected from the group consisting of H, C₂H₅, NO₂, OCH₃, CH₃, OC₂H₅, SO₂NH₂, CO₂CH₃, CN, CO₂C₂H₅, SO₂NHC₅H₄, Cl, Br, F, I.

19. The method of claim 18 wherein said recording medium comprises photoconductive pigment particles in an organic binder overcoated with a thermoplastic material
said photoconductive pigment comprising the composition having the general formula:

wherein R₁-R₄ are each selected from the group consisting of H, C₂H₅, NO₂, OCH₃, CH₃, OC₂H₅, SO₂NH₂, CO₂CH₃, CN, CO₂C₂H₅, SO₂NH₂H₂, Cl, Br, F, I.
CERTIFICATE OF CORRECTION

Patent No. 3,448,029 Dated June 3, 1969

Inventor(s) Lester Weinberger

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 40, after "are" insert --spontaneously--.
Column 3, line 14, "R_2" should read --R_1--.
Column 4, line 21, after "layer" insert"--of a blocking electrode material 12, which may be--.
Column 6, line 56, "about" should read --above--.
Column 11, line 28, "no" should read --not--.
Column 11, "Example XVII" should read --Example XXVII--.
Column 12, line 58, "bisphoslenol" should read --bisphenol--.
Column 12, line 64, "338,323" should read --388,323--.
Claim 2, line 6, delete ..."and"... and insert ...--with--... prior to ..."activating"...

SIGNED AND SEALED
MAR 3 1 1970

(SEAL)
Attests
Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents