ELECTRICALLY PHOTOSensitive PARTICLES USEFUL IN PHOTOELECTROPHORETIC AND XEROGRAPHIC IMAGING PROCESSES

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20 Claims

ABSTRACT OF THE DISCLOSURE

N - substituted 8,13 - dioxodinaphtho (2,1-b; 2',3'-d) - furan-6-carboxamides are described as new compositions of matter along with their use as electrically photosensitive particles in photoelectrophoretic and xerographic imaging process.

This invention relates in general to new compositions of matter and methods of using them. More specifically, the invention concerns the use of new electrically photosensitive pigments in electrophoretic imaging systems.

There has been recently developed an electrophoretic imaging system capable of producing color images which utilizes photoconductive pigment particles. This process is described in detail and claimed in copending applications Ser. Nos. 384,757 now U.S. Patent 3,384,565; 384,681 abandoned in favor of application Ser. No. 653,023 now U.S. Patent 3,384,566 and 384,680 abandoned in favor of application Ser. No. 518,041 now U.S. Patent 3,383,993, all filed July 23, 1964. In such an imaging system, variously colored light absorbing particles are suspended in a non-conductive liquid carrier. The suspension is placed between electrodes subjected to a potential difference and exposed to an image. As these steps are completed, selective particle migration takes place in image configuration, forming 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 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 originally described in U.S. Patent 2,297,691 to C. F. Carlson. Here, the photosensitive material must be an effective photoconducting insulator, i.e., must be capable of holding an electrostatic charge in the dark and dissi-

puting 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 photoconductive insulating surface coated 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 any given area is exposed, the charge being substantially retained in non-exposed areas, forming a latent electrostatic 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 image. Where the base sheet is relatively inexpensive, such as paper, the image may be fixed directly thereto as by heat or solvent fusing. Alternatively, the powder image may be transferred to a sheet of 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, and polyvinyl carbazol. While 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 Deformation" 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 photoconductive insulating material, which is then overcoated with a thermoplastic material. Alternatively, the photoconductive material may be dispersed in particulate form in the thermoplastic material and the mixture coated directly over 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 struck 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 surface folds or wrinkles are spontaneously 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 photoconductive 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 compositions for electrophotographic imaging processes which overcome the above noted deficiencies.

It is another object of this invention to provide novel photosensitive materials suitable for use in electrophotographic imaging processes.

It is another object of this invention to provide novel photosensitive compositions useful in electrophoretic imaging processes.

It is another object of this invention to provide novel compositions having an intense yellow color.

It is yet another object of this invention to provide a novel method of making a new yellow pigment.

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 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 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 providing novel compositions having the general formula:

$$
\text{O} \quad \text{E} \quad \text{R}_1 \quad \text{X}_1 \quad \text{X}_2 \quad \text{R}_2
$$

wherein:

- Each $\text{R}_1$ is selected from the group consisting of $\text{N}$ and $\text{C}$, from 1-3 $\text{R}_1$'s being $\text{N}$;
- Each $\text{X}_1$ is selected from the group consisting of $\text{H}$, $\text{CH}_3$, $\text{C}_2\text{H}_5$, $\text{NO}_2$, $\text{OCH}_3$, $\text{OC}_2\text{H}_5$, $\text{CN}$, $\text{SO}_2\text{NH}_2$, $\text{CO}_2\text{CH}_3$, $\text{CO}_2\text{C}_2\text{H}_5$, $\text{SO}_2\text{NHC}_2\text{H}_5$, $\text{Cl}$, $\text{Br}$, $\text{I}$ and mixtures thereof; and
- $n$ is a positive integer from 1-4.

The compositions of the general formula given above belong to the class of $N$-substituted 8,13-dioxonaphtho-(2,1-b; 2',3'-d)-furan-6-carboxamides wherein the substituent comprises amine substituted heterocyclic groups. These compositions may be made by reacting 2,3-dichloro-1,4-naphthoquinone with any suitable $N$-substituted amide of 2-hydroxy-3-naphthoic acid. Typical are those having the general formula:

$$
\text{O} \quad \text{H} \quad \text{R}_1 \quad \text{X}_1 \quad \text{X}_2 \quad \text{R}_2
$$

wherein:

- Each $\text{R}_1$ is selected from the group consisting of $\text{N}$ and $\text{C}$, from 1-3 $\text{R}_1$'s being $\text{N}$;
- Each $\text{X}_1$ is selected from the group consisting of $\text{H}$, $\text{CH}_3$, $\text{C}_2\text{H}_5$, $\text{NO}_2$, $\text{OCH}_3$, $\text{OC}_2\text{H}_5$, $\text{CN}$, $\text{SO}_2\text{NH}_2$, $\text{CO}_2\text{CH}_3$, $\text{CO}_2\text{C}_2\text{H}_5$, $\text{SO}_2\text{NHC}_2\text{H}_5$, $\text{Cl}$, $\text{Br}$, $\text{I}$ and mixtures thereof; and
- $n$ is a positive integer from 1-4.

The compositions produced by the above reaction have common characteristics of a brilliant, intense, yellow color; of insolubility in water and the common organic solvents, e.g., benzene, toluene, acetone, carbon tetrachloride, chloroform, alcohols, and aliphatic hydrocarbons; and of unusually high photosensitive response.

Of the compositions within the general formulation, the compositions having the general formula given above, N-2"-pyrylid - 8,13 - dioxonaphtho-(2,1-b; 2',3'-d)-furan-6-carboxamide, and N-2"-(1',3'-dazyl)-8,13-dioxonaphtho-(2,1-b; 2',3'-d)-furan-6-carboxamide are preferred for use in electrophoretic imaging processes since they are simply and economically synthesized, have especially pure color, and are most highly photosensitive. They have been found to give the most desirable combination of color and photosensitivity.

However, since the shade or the tone of the composition 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 compositions of this invention.

The following examples further define and describe methods of making the compositions of the present invention. Parts and percentages are by weight unless otherwise indicated. The examples below should be considered to illustrate various preferred embodiments of the invention.

**Example I**

About 11.4 parts of 2,3-dichloro-1,4-naphthoquinone is refluxed for about 3 hours with about 9.6 parts of N-2"-pyrylid-2-hydroxy-3-naphthamidine in boiling pyridine. The solution is cooled to room temperature and the product is removed by filtration and recrystallized from a mixture of equal parts by volume of methyl cellulose and alpha methyl formamide, yielding about 3.3 parts of N-2"-(1',3'-dazyl)-8,13-dioxonaphtho-(2,1-b; 2',3'-d)-furan-6-carboxamide having a melting point of about 334° C.

**Example II**

About 8.6 parts of 2,3-dichloro-1,4-naphthoquinone is refluxed for about 3 hours with about 10 parts of N-2"-(1',3'-dazyl)-2-hydroxy-3-naphthamidine in about 100 parts boiling pyridine. The solution is then cooled to room temperature. Ethyl alcohol is added until precipitation occurs. The precipitate is recrystallized from dimethyl formamide, yielding about 3.3 parts of N-2"-(1',3'-dazyl)-8,13-dioxonaphtho-(2,1-b; 2',3'-d)-furan-6-carboxamide.

**Example III**

About 11.4 parts of 2,3-dichloro-1,4-naphthoquinone is refluxed for about 3 hours with about 15 parts of N-2"-(1',3',5'-triazyl)-2-hydroxy-3-naphthamidine in about 100 parts boiling pyridine. The solution is then cooled to room temperature. Ethyl alcohol is added until precipitation occurs. The precipitate is recrystallized from dimethyl formamide, yielding 2,3-dioxonaphtho-(2,1-b; 2',3'-d)-furan-6-carboxamide.

In the table below, further examples are given for producing additional embodiments of the compositions of this invention. The table gives the number of the example in column 1, the parts by weight and name of the second reactant in column 2, and the parts by weight and name of the product in column 3. The processes used in preparing the compounds listed in the table are similar to that described in detail in Examples I and II above. In each example, about 22.5 parts of 2,3-dichloro-1,4-naphthoquinone is used as the first reactant.

In the chemical formulas as listed in the table below, X in column 2 represents the "2-hydroxy-3-naphthamidine" portion and Y in column 3 represents the "8,13-dioxonaphtho-(2,1-b; 2',3'-d)-furan-6-carboxamide" portion. Thus, for example, "N-2"-pyrylid-X" represents "N-2"-pyrylid-2-hydroxy-3-naphthocarboxamide"; "N-2"-(1',3'-dazyl)-Y" represents "N-2"-(1',3'-dazyl)-8,13-dioxonaphtho-(2,1-b; 2',3'-d)-furan-6-carboxamide"; etc.
TABLE I  

<table>
<thead>
<tr>
<th>Parts</th>
<th>Second reactant</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>N°°°pyridyl-X</td>
<td>N°°°pyridyl-Y</td>
<td>42.5 N°°°pyridyl-Y</td>
</tr>
<tr>
<td>N°°°pyridyl-X</td>
<td>N°°°pyridyl-Y</td>
<td>44.5 N°°°pyridyl-Y</td>
</tr>
<tr>
<td>N°°°pyridyl-X</td>
<td>N°°°pyridyl-Y</td>
<td>45.5 N°°°pyridyl-Y</td>
</tr>
<tr>
<td>N°°°pyridyl-X</td>
<td>N°°°pyridyl-Y</td>
<td>46.5 N°°°pyridyl-Y</td>
</tr>
</tbody>
</table>

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 covalently transparent glass 2 overcoated with a thin optically transparent layer 3 of tin oxide, commercially available under the name Nesa glass. This electrode shall 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 pigment 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 actinic electromagnetically radiated light. 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 hereinafter. 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 of a blocking electrode material 12, which may be Baryta paper. The pigment suspension 4 is exposed to the image to be reproduced while potential is applied across the blocking electrode 5 and injecting electrodes by closing 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 laminate over its top surface or by 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 alternate, 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 monochromatic 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 materials are decane, dodecane, N-teiradecane, paraffin, beeswax or other thermoplastic material, Sohio Odorless Solvent, (a kerosene fraction available from Standard Oil Company of Ohio), and Isopar-G (a long chain saturated aliphatic hydrocarbon available from Humble Oil Company of New Jersey.) 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 color 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 each behaves as one of different colors respond to different wavelengths 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 good 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 colored 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 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 removal of 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 component 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 tri-nix 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 cyan and magenta colored photosensitive pigment particles having the desired spectral response may be used with the yellow pigments of this invention to form a pigment mix in 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 mole 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 XXXIX-XLVI 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 2.5 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 step 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 XXXIX**

About 7 parts of N-2'-pyridyl-8,13-dioxodinaaphtho-(2,1-b; 2',3'-d)-furan-6-carboxamide is suspended in about 100 parts of Sohio Odorless Solvent 3440. The suspension is coated on the Nesa glass substrate and a negative potential is imposed on the roller electrode. The plate is 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 Table II, below.

**Example XL**

A test is run as in Example XXXIX 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 II for results.

**Example XLI**

A test is run as in Example XXXIX 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 II for results.

**Example XLIi**

A test is run as in Example XXXIX above, except that no color filter is used, thus exposing the plate to white light. See Table II for results.

**Example XLIiI**

About 7 parts N-2'(1',3'-diacyl)-8,13-dioxodinaaphtho-(2,1-b; 2',3'-d')-furan-6-carboxamide is suspended in about 100 parts Sohio Odorless Solvent 3440. The suspension is coated on the Nesa glass substrate and a negative potential is imposed on the roller electrode. The plate is exposed through a Wratten 29 filter and the neutral density step wedge filter, thus exposing the plate to red light. See Table II for results.

**Example XLIv**

A test is run as in Example XLIiI 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 II for results.

**Example XLV**

A test is run as in Example XLIiI 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 II for results.

**Example XLIvi**

A test is run as in Example XLIiI above, except that no Wratten filter is used, thus exposing the plate to white light. See Table II for results.

**TABLE II**

<table>
<thead>
<tr>
<th>Example</th>
<th>Written filter</th>
<th>Color light</th>
<th>Speed</th>
<th>Gamma</th>
<th>D max</th>
<th>D min</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXXIX</td>
<td>29 Red</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>XL</td>
<td>61 Green</td>
<td>do</td>
<td>do</td>
<td>do</td>
<td>do</td>
<td>do</td>
</tr>
<tr>
<td>XLII</td>
<td>47b Blue</td>
<td>300 f.e.</td>
<td>1.50</td>
<td>1.20</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>XLI</td>
<td>None White</td>
<td>200 f.e.</td>
<td>1.50</td>
<td>1.20</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>XLIi</td>
<td>29 Red</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>XLIiI</td>
<td>61 Green</td>
<td>do</td>
<td>do</td>
<td>do</td>
<td>do</td>
<td>do</td>
</tr>
<tr>
<td>XLIIV</td>
<td>47b Blue</td>
<td>700 f.e.</td>
<td>0.70</td>
<td>0.94</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>XLIvI</td>
<td>None White</td>
<td>700 f.e.</td>
<td>0.70</td>
<td>0.94</td>
<td>0.32</td>
<td></td>
</tr>
</tbody>
</table>

The electrophoretic sensitivity of the exemplary pigments to red, green, blue and white light is tested according to conventional photographic methods and the results are recorded in Table II, above. In the table, the first column lists the number of the test example. The Wratten filter used in each example between the light source and the Nesa plate is listed in column 2. The third
The pigments perform as a magenta pigment, Vulcan Fast Red BBE Toner, 35-2201, 3,3’-dimethoxy-4’,4’-biphenylbis(1” - phenyl - 3” - methyl - 4” - azo - 2” - perylene - 5” - one), C.I. No. 21200, available from Colway Colors; a cyan pigment, Cyan Blue, 3,3’-methylxy - 4’,4’ - diphenyl - bis(1” - azo - 2” - hydroxy - 3” - naptho phenyl), C.I. No. 21180, available from Harmon Colors, and as a yellow pigment, N-2’(3’-methyl) - pyridyl - 8,13 - dioxindolinophth (2’,1’-b; 2’,3’-d) - furan - 6 - carb oxamide. This tri-mix is exposed to a multi-colored image and produces a full color image of good density and color separation.

Example LI

The pigment suspension consists of a magenta pigment, Infostar Brilliant Scarlet Toner, 3,4,9,10-bis(N,N’-methylene-phenyl-imido) - perylene, C.I. No. 71140, available from Harmon Colors; a cyan pigment, Monolite Fast Blue GS, the alpha form of metal free phthalocyanine, C.I. No. 74100, available from the Arnold Hoffman Company, and a yellow pigment, N-2’(3’-methyl) - pyridyl - 8,13 - dioxindolinophth (2’,1’-b; 2’,3’-d) - furan - 6 - carb oxamide. A multi-colored image and produces a full color image of satisfactory density and good color separation.

Example LII

The pigment suspension consists of a magenta pigment, Calcium Litho Red, the calcium lake of an azo dye, 1-(2’-azophenanthrene-1’-sulfonic acid)-2-hydroxy-naphth, C.I. No. 15630, available from Colway Colors; a cyan pigment, Cyan Blue XX, the alpha form of copper phthalocyanine, available from Colway Colors; a yellow pigment, N-2’(1’3’-di azyl) - 8,13 - dioxindolinophth (2’,1’-b; 2’,3’-d) - furan - 6 - carb oxamide. This tri-mix is exposed to a multi-colored image and produces a full color image of good density and color separation.

The novel compositions of the general formula given above are also useful in xerographic imaging systems. For use in such processes, xerographic 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 photoconductive layer. As a third alternative to the above noted self-supporting layer, substrate supported layer, the photosensitive pigment-resin substrate may be used in the formation of multilayer structures adjacent a dielectric layer, similar to that shown by Golovin et al., in the publication entitled, “A New Electro photographic Process, Effects 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 cast the pigmented resin film on a substrate various supporting materials may be used. Suitable materials for this purpose may include aluminum, steel, brass, metalized or tin oxide coated glass, semiconductive plastics and resins, paper and any other convenient material. 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, must be more resistant than about 109 and preferably more than 1010 ohms/cm. under the conditions of xerographic use. Typical resins include thermoplastic such as polyvinylchloride, poly vinylacetate, polyvinylidenchloride, polystyrene, polybutadiene, polymethacrylate, parynes, polyacrylonitride, silicon resins, chlorinated rubber, and mixtures and copolymers thereof where applicable; and thermosetting resins such as epoxy resins including halogenated.
3,447,922

11 epoxy and phenoxy resins, phenolic, epoxy-phenolic copolymers, epoxy ureaformaldehyd copolymers, epoxy melamine formaldehyde copolymers and mixtures thereof where applicable. Other typical resins are epoxy esters, vinyl epoxy resins, tall-oil 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 sheet 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.

The pigment-resin-solvent 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 drawdown, dip coating, reverse roll coating, etc. Spraying in an electric field may be preferred for the smoothest finish and dip coating for convenience in the laboratory. The coating, drying, and 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 stoving according to approximately the same schedule as other baking enamels or the same resins and similar pigments for paint 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 the required individual purpose. Self-supporting films, for example, cannot usually be manufactured in thicknesses thinner than about 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 3 to 50 micron range. For certain compositions and purposes, it is desirable to provide an overcoating; this should usually exceed the thickness of the photoconductive coating, and preferably not about 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 indicated. All the materials tested below were charged, exposed and developed according to the conventional xerographic processes.

Xerographic plates for use as in the following examples are prepared as follows. Mixtures using specific pigments and resin binders are prepared by ball milling the pigment in a solution of a resinous binder and one or more solvents until the pigment is well dispersed. This is done by adding 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 homogenous dispersion. The cooling 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 an hour and then tested.

Example LI

The xerographic plate is initially prepared by mixing about 10 parts Lucite 2042, an ethyl methacrylate polyether available from Du Pont, about 90 parts benzene and about 2 parts N-2-pyridyl-8,13-dioxidinaphtho-(2,1-b; 2,3-d)-furan-6-carboxamide. The mixture is coated onto an aluminum substrate to a thickness of about 8 microns and cured. The plate is charged negative in the dark by means of a corona discharge to a potential of about 400 volts. The charged plate is exposed to a film positive for about 30 seconds by means of a high intensity, long wave, ultraviolet lamp (1680 microwatts/cm² of 3660 A.U. radiation at a distance of 18 inches). The latent electrostatic image is developed by cascading Xerox 1824 toner over the plate. The powder image is then erased by evaporatively transferring to a receiving sheet and heat fused. The image on the receiving sheet is of excellent quality and corresponds to the original. The plate is wiped clean of any residual toner and reused as in the above manner.

Example LIV

A xerographic plate is prepared by initially mixing about 10 parts Lucite 2042, about 90 parts benzene and about 2 parts N-4-(1";3";5";di-azoyl)-8,13-dioxidinaphtho-(2,1-b; 2,3-d)-furan-6-carboxamide. The mixture is coated onto an aluminum substrate to a thickness of about 8 microns and cured. The plate is charged negative in the dark by means of a corona discharge to a potential of about 40 volts. The charged plate is exposed to a film positive for about 45 seconds to a light and shadow image using a Simmons 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. The latent electrostatic image is then developed by cascading Xerox 1824 toner over the plate. The powder image on the plate is electrostatically transferred to a receiving sheet and heat fused. The image on the receiving sheet is of good quality and corresponds to the original. The plate is wiped clean of any residual toner and reused as in the above described manner.

The third electrophotographic imaging process in which the above listed novel 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 processes 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 softening point. The image may be erased by reheating the layer in a charge free condition to its softening point.

(2) 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.
(3) 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 solvent softening. This image may be set by returning the layer to its pre-softened condition.

(4) Any of the methods described in detail in copending applications 193,277 now U.S. Pat. 3,196,011, 232,494 now U.S. Pat. 3,244,083 and 388,322 now abandoned in favor of application Serial No. 670,824 filed May 8, 1962; Oct. 13, 1962 and Aug. 7, 1964, respectively, may be used in the process of this invention. For example, the methods of forming the frost or relief image may vary depending upon the intended use of the resulting product. In certain situations, the heat deformable layer may be pretreated 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 or oligomers. Any suitable polymer 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, methyl-styrene, polyvinylmethyl styrene, chlororated 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, butylmethyl-acrylate-styrene polymers, butylmethacrylate-alcoholated styrene copolymers, styrene-methacrylate-butyadiene terpolymers; organo-polysiloxanes such as polydiphenylsiloxane; polymers such as acrylic esters, bisphenol-A type polymers; bisphenol-A copolymers; complex hydrocarbon polymers such as hydrogenated polyethylene and other mixtures and copolymers thereof. If desired, deformation characteristics of the films may be improved by incorporating on the surface thereof of film surface skins as disclosed in copending application 388,323 filed Aug. 7, 1964.

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 heat deformable imaging according to the present invention.

Broadly, the heat 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 LVI

A plate is prepared by initially mixing about 10 parts Lucite 2042, an ethyl methacrylate polymer available from Du Pont, about 90 parts benzene and about 2 parts N-2″-pyridyl-8,13 -dioxodinaphtho-(2,1-b;2′,3′-d)-furan-6-carboxamide. 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 Piccollex 100-A (a polyvinylchloride resin obtained from Pennsylvania Industrial Chemicals Company). 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/cm.² if 3600 A.U. radiation at a distance of 18 inches). The latent electrostatic image 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 frost image corresponding to the original appears.

Example LVII

A plate is prepared by initially mixing about 10 parts Lucite 2042, about 90 parts benzene and about 2 parts N-4″(1″,3″,5″ -diaryl) -8,13 -dioxodinaphtho -(2,1-b;2′,3′-d)-furan-6-carboxamide. 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 Piccollex 100-A. The composite plate is charged, exposed, and developed as in Example LVI above. Again, a frost pattern in image configuration is observed.

Example LVIII

A plate is prepared by initially mixing about 10 parts Lucite 2042, about 90 parts benzene and about 2 parts N,2″(1″,3″,5″ -triaryl) -8,13 -dioxodinaphtho -(2,1-b;2′,3′-d)-furan-6-carboxamide. 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 Stycelite Ester No. 10 available from Hercules Powder Company. 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 for about 45 seconds to a light and shadow image using a Simmons Omega D3 enlarger equipped with a tungsten light source operating at 2950 K. color temperature. Illumination level incident on the plate is about 2.8 foot candles as measured with a Weston Illumination Meter Model No. 756. The latent electrostatic image is developed by placing the plate on a platen heated to a temperature of about 70°C. As the softening temperature of the overcoating is reached, a frost pattern in image configuration again 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.

The novel compositions of this invention are further useful as pigments for paints, varnishes, etc., and for plastic molding and coating compositions. They are useful as pigments in paper making processes when a yellow colored paper is desired. The pigments may also be dispersed in synthetic filament forming materials useful in the production of synthetic textiles. The compositions have further uses in certain insecticides, herbicides and fungicides.

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. A composition having the general formula:

\[
\text{H R-R Xn X O -N-c. R n 2 & R-R}
\]

wherein:

each R is selected from the group consisting of N and C, from 1-3 R's being N;
each X is selected from the group consisting of H, CH.
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CH₃, NO₂, OCH₃, OC₆H₅, CN, SO₂NH₂, CO₂CH₃, CO₂C₆H₅, SO₃NH₂CH₃, Cl, F, Br, I; and
n is a positive integer from 1–4.

2. A composition having the general formula:

wherein:
each R is selected from the group consisting of N and C, from 1–3 R’s being N.


4. N-2'‘(1‘,3’-diaryl) - 8,13 - dioxoaminaphtho-(2,1-b;
2’,3’-d)-fur-an-6-carboxamid.

5. N-2'(1‘,3’‘,4’-triaryl) - 8,13-dioxoaminaphtho-2,1-b;
2’,3’-d)fur-an-6-carboxamid.

6. A coating composition comprising a hardenable car-
rier having dispersed therein a pigment having the general formula:

wherein:
each R is selected from the group consisting of N and C, from 1–3 R’s being N;
each X is selected from the group consisting of H, CH₃,
C₆H₅, NO₂, OCH₃, OC₆H₅, CN, SO₂NH₂, CO₂CH₃,
CO₂C₆H₅, SO₃NH₂CH₃, Cl, F, Br, I; and
n is a positive integer from 1–4.

7. A coating composition comprising a hardenable car-
rier having dispersed therein N-2'(1‘,3’‘-diaryl)-8,13-dioxoaminaphtho-(2,1-b;2’,3’-d)-fur-an-6-carboxamid.

8. The method of electrophoretic imaging comprising
subecting a layer of a suspension to an applied electric
field between at least two electrodes, at least one of which is
at least partially transparent and simultaneously expos-
sing said suspension to an image through said partially
transparent electrode with activating electromagnetic
radiation whereby an image is formed on at least one of
said electrodes; said suspension comprising a plurality of
finely divided photosensitive particles of at least one
color, at least one of said particles comprising a compo-
sition having the general formula:

wherein:
each R is selected from the group consisting of N and C, from 1–3 R’s being N;
each X is selected from the group consisting of H, CH₃,
C₆H₅, NO₂, OCH₃, OC₆H₅, CN, SO₂NH₂, CO₂CH₃,
CO₂C₆H₅, SO₃NH₂CH₃, Cl, F, Br, I; and
n is a positive integer from 1–4.

9. 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
at least partially transparent and simultaneously expos-
sing said suspension to an image through said partially
transparent electrode with activating electromagnetic
radiation whereby an image is formed on at least one of
said electrodes; said suspension comprising a plurality of
finely divided photosensitive particles of at least one
color, at least one of said particles comprising N-2'(1‘,
3’‘,5’-triaryl) - 8,13 - dioxoaminaphtho - (2,1 - b;
2’,3’- d) fur-an-6-carboxamid.

10. 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
at least partially transparent and simultaneously expos-
sing said suspension to an image with activating electromagnetic
radiation whereby an image is formed on at least one of
said electrodes; said suspension comprising a plurality of
finely divided photosensitive particles of at least one
color, at least one of said particles comprising N-2'(1‘,
3’‘,5’-triaryl) - 8,13 - dioxoaminaphtho - (2,1 - b;
2’,3’- d) fur-an-6-carboxamid.

11. 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
at least partially transparent, said suspension comprising a plurality of
finely divided photosensitive particles of at least two different colors in an insulating carrier liquid, the particles of each color comprising a photosensitive pigment whose principal light absorption bands substantially coincides with its principal photosensitive response, simultaneously exposing said suspension to a light image through said transparent electrode and then separating said electrodes whereby an image is formed on the surface of at least one of said electrodes; the particles of
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one color comprising compositions having the general formula:

wherein:
each R is selected from the group consisting of N and C, from 1-3 R's being N;
each X is selected from the group consisting of H, C_{2}H_{5}, NO_{2}, OCH_{3}, OC_{2}H_{5}, CN, SO_{3}NH_{2}, CO_{3}CH_{7}, CO_{3}CH_{4}, SO_{3}NHCH_{2}CH_{3}, Cl, F, Br, I; and
n is a positive integer from 1-4.

13. 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 at least partially 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 principal light absorption bands substantially coincides with its principal photosensitive response, simultaneously exposing said suspension to a light image through said transparent electrode and then separating said electrodes whereby an image is formed on the surface of at least one of said electrodes; the particles of one color comprising the general formula:

N - 2'- pyridyl-8,13-dioctodinaphtho - (2,1-b; 2',3'-d) - furan-6-carboxamide.

14. 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, 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 principal light absorption bands substantially coincides with its principal photosensitive response, simultaneously exposing said suspension to a light image and then separating said electrodes whereby an image is formed on the surface of at least one of said electrodes; the particles of one color comprising the general formula:

wherein:
each R is selected from the group consisting of N and C, from 1-3 R's being N;
each X is selected from the group consisting of H, C_{2}H_{5}, NO_{2}, OCH_{3}, OC_{2}H_{5}, CN, SO_{3}NH_{2}, CO_{3}CH_{7}, CO_{3}CH_{4}, SO_{3}NHCH_{2}CH_{3}, Cl, F, Br, I; and
n is a positive integer from 1-4.

15. 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, 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 principal light absorption bands substantially coincides with its principal photosensitive response, simultaneously exposing said suspension to a light image and then separating said electrodes whereby an image is formed on the surface of at least one of said electrodes; the particles of one color comprising the general formula:

wherein:
each R is selected from the group consisting of N and C, from 1-3 R's being N;
each X is selected from the group consisting of H, C_{2}H_{5}, NO_{2}, OCH_{3}, OC_{2}H_{5}, CN, SO_{3}NH_{2}, CO_{3}CH_{7}, CO_{3}CH_{4}, SO_{3}NHCH_{2}CH_{3}, Cl, F, Br, I; and
n is a positive integer from 1-4.

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

wherein:
each R is selected from the group consisting of N and C, from 1-3 R's being N;
each X is selected from the group consisting of H, C_{2}H_{5}, NO_{2}, OCH_{3}, OC_{2}H_{5}, CN, SO_{3}NH_{2}, CO_{3}CH_{7}, CO_{3}CH_{4}, SO_{3}NHCH_{2}CH_{3}, Cl, F, Br, I; and
n is a positive integer from 1-4.

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

wherein:
each R is selected from the group consisting of N and C, from 1-3 R's being N;
each X is selected from the group consisting of H, C_{2}H_{5}, NO_{2}, OCH_{3}, OC_{2}H_{5}, CN, SO_{3}NH_{2}, CO_{3}CH_{7}, CO_{3}CH_{4}, SO_{3}NHCH_{2}CH_{3}, Cl, F, Br, I; and
n is a positive integer from 1-4.

18. A method of forming a latent electrostatic charge pattern on a deformable layer which comprises charging said layer, exposing said layer to a pattern of activating electromagnetic radiation, dissipating at least a portion of the charge on said layer to thereby form a latent electrostatic charge pattern corresponding to said pattern of activating electromagnetic radiation; said layer comprising an organic binder and a photosensitive pigment composition having the general formula:
19. A method for forming an image on a surface deformable recording medium which comprises electrostatically charging a recording medium, said recording medium comprising photoconductive pigment particles in an organic binder coated on a supporting substrate and overcoated with a thermoplastic material, exposing said medium to a pattern of light and shadow and maintaining said surface 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, said photoconductive pigment comprising the composition having the general formula:

\[ \text{wherein: each } R \text{ is selected from the group consisting of } N \text{ and } C, \text{ from } 1-3 \text{ R's being } N; \]
\[ \text{each } X \text{ is selected from the group consisting of } H, \text{ CH}_3, \text{ NO}_2, \text{ OCH}_3, \text{ AC}_2\text{H}, \text{ CN, SO}_2\text{NH}_2, \text{ CO}_2\text{CH}_3, \]
\[ \text{CO}_2\text{C}_2\text{H}_5, \text{SO}_2\text{NH}_2\text{C}_2\text{H}_5, \text{Cl, Br, I; and } n \text{ is a positive integer from } 1-4. \]

20. A method for forming an image on a surface deformable recording medium which comprises electrostatically charging a recording medium, said recording medium comprising photoconductive pigment particles in a thermoplastic binder coated on a supporting substrate, exposing said medium to a pattern of light and shadow and maintaining said surface 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, said photoconductive pigment comprising the composition having the general formula:

\[ \text{wherein: each } R \text{ is selected from the group consisting of } N \text{ and } C, \text{ from } 1-3 \text{ R's being } N; \]
\[ \text{each } X \text{ is selected from the group consisting of } H, \text{ CH}_3, \text{ NO}_2, \text{ OCH}_3, \text{ AC}_2\text{H}, \text{ CN, SO}_2\text{NH}_2, \text{ CO}_2\text{CH}_3, \]
\[ \text{CO}_2\text{C}_2\text{H}_5, \text{SO}_2\text{NH}_2\text{C}_2\text{H}_5, \text{Cl, Br, I; and } n \text{ is a positive integer from } 1-4. \]
UNIVERS STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,447,922 Dated June 3,

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 4, delete lines 35 and 36 and insert — methyl-naphthalene. The product comprises about 4.5 parts N-2" -pyridyl- 8, 13 -dioxodinaphtho - (2,1-b; 2; 3'-d)-furan —

Column 13, line 60 "(2,1-2';3'-d)" should read — (2,1-b; 2',3'-d) —

SIGNED AND SEALED
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(SEAL)
Attest:
Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents