METHOD OF PHOTOELECTROPHORETIC IMAGING

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32 Claims. (Cl. 204—181)

ABSTRACT OF THE DISCLOSURE

An electrophoretic imaging system is disclosed in which a layer of a suspension comprising electrically photosensitive particles in a liquid carrier is placed between a pair of electrodes, one of which is transparent, an electric field is imposed across the suspension and the suspension is exposed to an image through the transparent electrode whereby an image of migrated particles forms on at least one electrode.

Background of the invention

This invention relates in general to a novel imaging system and more specifically, to an imaging system based on the phenomenon of photolecetrophoresis. This application is a continuation-in-part of my copending application, Ser. No. 384,681, filed July 23, 1964 and now abandoned.

Although many photographic systems are known today, such as, for example, processes based on photolytic reduction of silver salts or chromate compounds, photolysis of the ferric ion to the ferrous ion, the use of phototropic compounds, the diazo coupling reaction, various thermo-graphic techniques, photobleaching of dyes, photopolymerization, etc., all of the known systems of photography suffer from one shortcoming or another. For example, some require expensive and complex initial preparation of the photosensitive media while others suffer from deficiencies in resolution capabilities, photographic speeds, spectral sensitivity and the like. In addition to the above-mentioned shortcomings of many of the present-day photographic systems, additional processing is generally required to produce a visible image from the latent image produced on the photosensitive media after its exposure to light. In conventional silver halide systems, for example, this generally requires developing and fixing of the negatives, printing the negative on a printing paper followed by developing, fixing and drying of the positive print.

Now, in accordance with the present invention, there is described an imaging system in which one or more types of photosensitive radiant energy absorbing particles which are held to be charge when suspended in a substantially nonconductive liquid carrier are suspended in such a liquid, placed in an electroded system and exposed to an image. When these steps are completed, particle migration takes place in image configuration providing a visible image at one or both of the electrodes. The system employs as the principal component of the particles pigment which are themselves photosensitive and which apparently undergo a net change in charge polarity upon exposure to activating radiation, by interaction with one of the electrodes. No other significant photosensitive elements or materials are required, making for a very simple and inexpensive imaging technique. Mixtures of two or more differently colored particles are used to secure various colors of images and imaging mixes having different spectral responses. Pigments in these mixes may have either separate or overlapping spectral response curves and may even be used in subtractive color synthesis, as described in copending application Ser. No. 384,737, filed July 23, 1964.

Although imaging systems based on particle migration techniques have been suggested in the prior art as described, for example, in U.S. Patent 2,940,847 to Kaprelian, these systems have proven so light insensitive, produce such poor images and are so complex and difficult to manufacture that they have never been accepted commercially. These prior art systems employ complex particles including at least two and frequently more layers of various different materials including, for example, photoconductive cores with varying high resistivity light filtering overcoatings and sometimes include glass cores, encapsulated dyes and similar components, which were previously thought to be necessary to provide light filtering action, to prevent particle interaction and oscillation in the system and perform other functions. It has, however, been discovered quite unexpectedly and surprisingly in accordance with the present invention that this complex layer structure is not only unnecessary but is even undesirable and that instead, simple particles made up primarily of colored photosensitive pigments may be used to produce excellent results under the conditions described hereinafter.

Summary of the invention

Accordingly, it is an object of this invention to define a novel and extremely uncomplicated imaging system.

An additional objective of the invention is to define a novel imaging system capable of direct positive imaging.

Still another objective of the invention is to define a novel imaging system for producing images in one or more colors.

Yet a further objective of this invention is to describe novel imaging compositions useful in the system of the aforesaid objectives.

Brief description of the drawings

The above and still further objects, features, and advantages of the present invention will become apparent upon consideration of the following detailed disclosure of the invention, especially when taken in conjunction with the accompanying drawings where:

FIGS. 1 and 1a are side views of simple exemplary systems for carrying out the steps of the invention;

FIGS. 2a, 2b, 2c, and 2d are broken side diagrammatic views of consecutive occurrences which apparently take place during the operation of the imaging process. The sizes and shapes of elements of the drawings should not be considered as actual sizes or even proportional to actual sizes because many elements have been purposely distorted in size or shape in order to more fully and clearly describe the invention.

Referring now to FIGURE 1, there is seen a transparent electrode generally designated 11 which, in this exemplary instance, is made up of a layer of optically transparent glass 12 overcoated with a thin optically transparent layer 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 11 is a thin layer of finely divided electrically photosensitive particles dispersed in a substantially insulating liquid carrier. During this initial part of the description of the invention, the term "electrically photosensitive" may be thought of as any 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 electromagnetic radiation. A detailed theoretical explanation of the apparent mechanism of operation of the invention and the "electrically photosensitive" nature of the particles is given below. The liquid suspension 14 may also con-
tain 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. Above the liquid suspension 14 is a second electrode 16 which is connected to one side of the potential source 17 through a switch 18. The opposite side of potential source 17 is connected to the injecting electrode 11. When switch 18 is closed, an electric field is applied across the liquid medium charge 14 between electrodes 11 and 16. An image projector made up of a light source 19, a transparency 21, and a lens 22 is provided to expose the dispersion 14 to a light image of the original transparency 21 to be reproduced. It should be noted at this point that injecting electrode 11 need not necessarily be optically transparent but that instead, electrode 16 may be optically transparent and exposure may be made through it from above as seen in FIGURE 1.

The embodiment shown in FIGURE 1a uses identical numerals to identify identical parts of the device and is the same as the FIGURE 1 embodiment of the invention except for the fact that electrode 16 is made in the form of a roller 23 having a conductive central core 24 connected to the potential source 17. The core is covered with a layer of a blocking electrode material 26, which may, for example, be baryta paper. In both the FIGURE 1 and FIGURE 1a embodiments of the invention, the particle suspension is exposed to the image to be reproduced while potential is applied across the blocking and injecting electrodes by closing switch 18. In the FIGURE 1a embodiment of the invention, roller 23 is caused to roll across the top surface of injecting electrode 11 with switch 18 closed during the period of image exposure. This light exposure causes exposed particles originally attracted to electrode 11 to migrate through the liquid and adhere to the surface of the injecting electrode material 26 leaving behind a particulate image on the injecting electrode surface which is a positive duplicate of the original transparency 21. Similarly, in the FIGURE 1 embodiment, electrode 16 may be removed, after exposure, from the surface of the pigment suspension 14 whereupon the relatively volatile carrier liquid evaporates off leaving behind the particulate image. This image may then be 80 fixed in place, as for example, by placing a lanimation over its top surface or by virtue of a dissolved binder material in the carrier liquid such as paraffin wax or other suitable binders that come 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.

In FIGURE 2a through 2d show in detail a proposed theoretical operating mechanism for the system with the particle size and carrier liquid thickness greatly exaggerated for purposes of illustration. Since the system has been experimentally shown to be operative, there is, of course, no intention to limit the invention to this theory of operation which is only given for clarification. In these figures, identical numerals have been used to identify parts of the system which are identical with those in FIGURES 1 and 1a. Referring now to FIGURE 2a, it is seen that the particle dispersion generally identified as 14 consists of the substantially insulating carrier liquid 27 having charged particles 28a, 28b, 28c, etc., suspended therein. The particles 28 bear a net electrostatic charge when suspended in the carrier liquid 27 which is believed to be related to the triboelectric relationship of the particles and liquid. The charges are trapped or bound either within the body of the particles or at their surfaces. The net charge on the particles may be either positive or negative; however, in this instance, an encircled negative charge in each particle has been employed to diagrammatically indicate that trapped negative charge carriers give that particular particle a net negative electrostatic charge. When switch 18 is left in the open condition and no potential is applied across electrodes 11 and 16 in the system as seen in FIGURE 2a, the positively charged particles merely assume random positions in the liquid carrier 27. However, when switch 18 is closed thereby rendering the conductive surface 13 of electrode 11 positive with respect to the back surface of blocking electrode 16, negatively charged particles within the system tend to move toward electrode 11 while any positively charged particles in the system would move toward blocking electrode 16. The existence of any positively charged particles within the system and their movement therein will temporarily be disregarded so as to facilitate the explanation of the movement of negatively charged particles in the carrier liquid. Since the particles 28 are, in the absence of actinic radiation, nonconductive, they come down into contact with or closely adjacent to injecting electrode 11 and remain in that position under the influence of the applied electric field until they are subjected to exposure to activating electromagnetic radiation. In effect then, these particles are bound at the surface of the injecting electrode 11 until exposure takes place because particles 28 are sufficiently nonconductive in the suspension in their unexposed condition to prevent the injection of positive charge from the surface 13 of the electrode 11 into them. Positively charged 85 bound on the surface 13 make up the potential imaging particles for the final image to be reproduced thereon.

When photons of light such as 31 in FIGURE 2c are produced as, for example, by the projector which exposes the system to the image being reproduced, they are absorbed by the photosensitive pigment in particle 28b and "create" hole-electron pairs of charge carriers within the particle by raising them to a conductive energy band. Since the charge carriers are newly formed by the photons of light 31, as shown in FIGURE 2c, they have not had a chance to become trapped in charge traps within the body of the particle 28b as was the encircled negative charge carrier. Accordingly, these newly formed charge carriers may be considered as mobile in nature and have been represented by unencircled plus and minus signs. Since an electric field is applied across the particles by the potential applied across electrode 16 and conductive surface 13 of electrode 11, the hole-electron pairs created within these particles are caused to separate before they can recombine, with negative charge carriers moving towards surface 13 while positive charge carriers move up toward electrode 16. Since the charge carrier as initially formed are in a mobile condition, the negative charge carriers near the pigment-electrode interface can move across the very short distance out of the particle 28b to the surface 13 as indicated by the small arrow, leaving the particle with a net positive charge. Since particle 28b now carries a net positive charge, it is repelled away by the positive surface 13 of electrode 11 and attracted to negative blocking electrode 16, moving as indicated by arrow 32 in FIGURE 2d. Accordingly, all particles such as 28b on the surface 13 which are exposed to electromagnetic radiation of a wavelength to which they are sensitive (that is to say, a wavelength which will cause the formation of hole-electron pairs within the particles) move away from surface 13 up to the surface of electrode 16, leaving behind those particles such as 28c which are either not exposed at all or not exposed to electromagnetic radiation to which they are sensitive. Particles reaching the blocking electrode surface 16 adhere thereto since this surface is substantially insulating and resists migration of charge from the particles. Consequently, if all particles in the system are sensitive to one wavelength of light or another and the system is exposed to an image with that wavelength of light, a positive image will be formed on the surface of electrode 13 by the subtraction of bound particles from its surface in exposed areas leaving behind bound par-
articles in unexposed areas. The system is also capable of creating a photographically negative image on surface 16 since only particles in exposed areas move up to that surface. As particles such as 280 move up through the liquid carrier 27 from surface 13 towards electrode 16, 5 it is believed that the new charge carriers enter charge carrier traps and this has been indicated diagrammatically by showing the holes enclosed within circles in FIGURE 2d. Accordingly, the particle now contains one trapped electron and two trapped holes giving it a net charge of plus 1.

As should be clear at this point in the disclosure, there are certain preferred properties for the electrodes 11, 16. These are that electrode 11 will preferably be capable of accepting injected electrons from bound particle 280 when it is exposed to light so as to allow for a net change in the charge polarity on the particle and that electrode 16 will preferably be a blocking electrode which is incapable of injecting electrons into particle 280 at a more than a very slow rate when they come into contact with the surface of the electrode 16. Obviously, if all polarities in the system are reversed, electrode 11 will preferably be capable of accepting injected holes from bound particles upon exposure to light and electrode 16 would preferably be a blocking electrode incapable of injecting holes into the surface of the net charge will, of course, vary depending upon the inter-electrode gap and on the thickness and type of blocking material used on the blocking electrode surface. For the very highest image quality, the optimum field is at least about 2,000 volts per mil. The upper limit of field strength is limited only by the breakdown potential of the suspension and blocking material. Fields below about 300 volts per mil, while capable of producing images, generally produce images of low density and of irregular density across the image.

The field here is found by dividing the inter-electrode gap into the potential applied between the electrodes. The field is assumed to be applied across this gap. Thus, where the two electrodes are spaced about 1 mil apart, a potential of about 300 volts applied between the blocking electrode and the injecting electrode surface will produce a field across the suspension of about 300 volts per mil.

Depending upon the particular use to which the system is to be put, the liquid suspension 14 may contain 1, 2, 3, or even more different particles of various colors and having different ranges of spectral response. Thus, for example, in a mono-chromatic system, the particles included in the image liquid 14 and may be virtually any color in which it is desired to produce the final image as gray, black, blue, red, yellow, etc. and the particular point or range of its spectral response is relatively immaterial as long as it shows response in some region of the visible spectrum which can be matched by a convenient exposure source. There should, however, be substantial coincidence between the primary spectral absorption range and the primary photosensitive response range of the particles to insure high photographic sensitivity in the system. In fact, in a monochromatic system, the pigment may vary in response from one with a very narrow response band all the way up to one having panchromatic response. In polychromatic systems, the particles may be selected so that particles of different colors respond to different wave lengths in the visible spectrum, thus allowing for color separation. It should be noted, however, that this separation of spectral response is not required in all instances and in some cases may actually be undesirable. Thus, for example, in a monochromatic black and white system where it is desirable to produce very intense black images, it may be preferred to produce this result by employing two or more differently colored pigments in the system, when combined will produce a black image. In this latter instance, considerable overlap and even coincidence of the
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1-phenyl-3-(p-methoxy styryl)-5-(p-methoxy-phenyl)-
pyrazole;
1-methyl-2-(3',4'-dihydroxy-methyleylene-phenyl) -
benzimidazole;
2-(4'-dimethylaminophenyl)-benzoxazole;
2-(4'-methoxyphenyl)-benzthiazole;
2,5-bis[p-aminophenyl-(1)]-1,3,4-oxidiazole;
4,5-diphenyl-Imidazolone;
3-amino-carbazole;
copolymer mixtures thereof.

Other materials include organic donor-acceptor (Lewis
acid-Lewis base) charge-transfer complexes made up of
aromatic donor resins such as phenolaldehyde resins,
phenoxyes, epoxies, polycarbonates, urethanes, styrene or
the like, complexed with electron acceptors such as 2,4,7-
trinitro-9-fluorenone; 2,4,5,7-tetranitro-9-fluorenone; pic-
ric acid; 1,3,5-trinitro benzene; chloranil; 2,5-dichloro-
benzoquinone; anthraquinone-2-carboxylic acid, 4-nitro-
phenol; maleic anhydride; metal halides of the metals and
metalloids of Groups I-B and II-VIII of the Periodic
Table including for example, aluminum chloride, zinc
chloride, ferric chloride, magnesium chloride, calcium
iodide, silver bromide, chromic acid, arsenic tri-
iodide, magnesium bromide, stannous chloride etc.; boron
halides, such as boron trifluorides; ketones such as benzo-
phenone and anisil, mineral acids such as sulfuric acid;
organic carboxylic acids such as acetic acid and maleic
acid, succinic acid, citric acid, sulphonic acid, such as
4-toluene sulfonic acid and mixtures thereof. In addi-
tion to the charge transfer complexes, it is to be noted
that many other of the above materials may be further
sensitized by the charge transfer complexing technique
and that many of these materials may be dye-sensitized to
narrow, broaden or heighten their spectral response curves.

As stated above, any suitable particle structure may be
employed. Typical particles include those which are
made up of only the pure photosensitive material or a
sensitized form thereof, solid solutions or dispersions of
the photosensitive material in a matrix such as thermo-
plastic or thermosetting resins, copolymers of photosensi-
tive pigments and organic monomers, multilayers of par-
ticles in which the photosensitive material is included
in one of the layers and where other layers provide light
filtering action in an outer layer or a fusible or solvent
softenable core of resin or a core of liquid such as dye
or other marking material or a core of one photosensitive
material coated with an overlay of another photosensi-
tive material to achieve broadened spectral response.

Other photosensitive structures include solutions, disper-
sions, or copolymer of one photosensitive material in
another with or without other photosensitively inert ma-
terials. While the above structural and compositional
variations are useful, it is preferred that each particle be
primarily composed of an electrically photosensitive pig-
ment, such as those listed above, wherein the pigment is
both the primary electrically photosensitive ingredient
and the primary colorant for the particle. These particles
have been found to give optimum photographic sensi-
tivity and highest overall image quality in addition to
being simple and economical to prepare. Of course, it
may often be desirable to include other ingredients, such
as spectral or electrical sensitizers or secondary colorants
and secondary electrically photosensitive materials.

Regardless of whether the system is employed to re-
produce a monochromatic or a polychromatic image, it is
desirable to use pigment particles which are relatively
small in size because smaller particles produce better and
more stable pigment dispersions in the liquid carrier and,
in addition, are capable of producing images of higher
resolution that would be possible with particles of larger
sizes. In general, best results have been obtained with
particles having an average diameter of up to about 5
microns. While satisfactory images may be obtained with
larger particles, the images tend to be splotchy in appear-
ance and to have low density. For optimum image density
and uniformity of density across the image, particles hav-
ing a diameter up to about 1 micron should be used. Even
where the pigments are not commercially available in
small particle sizes, the particle size may be reduced by
conventional techniques such as extended ball milling or
the like. When the particles are suspended in the liquid
carrier, they may take on a net electrostatic charge so that
they may be attracted towards one of the electrodes in the
system depending upon the polarity of the charge with
respect to that of the electrodes. It is not necessary that
the particles take on only one polarity of charge but in-
stead the particles may be attracted to both electrodes.
Some of the particles in the system may also be ac-
towards the "injecting" electrode while others move to-
wards the "blocking" electrode with this type of system;
however, this particle migration takes place uniformly over
the whole area covered by the two electrodes and the ef-
tect of imagewise, exposure-induced migration is super-
imposed upon it. Clearly then, the apparent bipolarity
of the suspensions in no way affects the imaging capability
of the system except for the fact that it subtracts some
of the particles uniformly from the system before image-
wise modulation of the particle migration takes place. In
other words, the above behavior causes a portion of the
suspended particles to be removed from the system as es-
tential image-formers. The effective subtraction of some
of these particles as potential image formers in the system
is easily overcome by merely forming an initial suspension
of particles containing a sufficiently high particle concen-
tration so that the system is still capable of producing in-
tense images. It also has been found that with some sus-
pensions of this type, either polarity of potential may be
applied to the electrodes during imaging. Although some
of the photosensitive pigment materials used in this inven-
tion may be used in conventional dry modes of operation,
It is believed that a different type of photoresponsive mech-
anism is involved because it has generally been found that
the spectral response of the materials is much narrower and
their sensitivity is much higher when they are used in the
liquid carrier structure of this invention. Also, in dry sys-
tems Van der Waals forces have a serious detrimental ef-
fect on imaging with particles smaller than about 10
microns. Surprisingly, in the liquid carrier of the present
invention particles smaller than 1 micron may be used
without significant interference due to Van der Waals
forces.

The addition of small amounts (generally ranging from 
.5 to 3 mol percent) of electron donors or acceptors to
the suspensions with the choice depending upon whether
the particles attracted to the "injecting" electrode are posi-
tive or negative respectively has imparted significant in-
creases in system photosensitivity as described in the ex-
amples. This effect is believed to be caused either by the
scavenging of free charge carriers from the system or from
an initial charge build up on the surface of the particles.
For further details of electrically sensitizing this system,
see copending application Ser. No. 566,846, filed July 21,
1966.

As stated above, once the particle image is formed on
one of the electrodes, it may be fixed thereon by as spray-
ing a binder on it, laminating an overlay on it or by in-
cluding a binder in solution in the liquid suspending me-
dium. In most instances, however, it will be found prefer-
able to transfer the image from the electrode and fix it on
another surface so that the electrode may be reused. Such
a transfer step may be carried out by adhesive pickoff with
an adhesive tape such as Scotch brand adhesive tape or
preferably, by electrostatic field transfer. Electro-
static transfer may, for example, be carried out by carry-
ning out the imaging procedure described in connection
with FIGURE 1a and then passing a second roller over the
particle image formed on electrode 11 held at a poten-
tial opposite in polarity to that of the first electrode.
If the second electrode roller is covered with a baryta
made through the filter. Thus, where one step is visible in the image, sensitivity is one; where two are visible, it is two; where three are visible, it is four; where four are visible, it is eight, etc.

In addition to the sensitivity tests, each of the compositions listed below is suspended in the carrier liquid and exposed to a conventional black-and-white transparency containing line copy images using white light. Each of the compositions listed below produces an image of good quality, with a positive image conforming to the original formed on the NESA glass surface and a negative image formed on the roller surface.

In these examples, the particles are homogeneous, each made up of a single composition as follows:


Example V.—Duol Carmen, the calcium lake of 1-(4’-methylazo)benzene-2’-sulfonic acid)-2-hydroxy-3-naphtholic acid, C.I. No. 15830, available from E. I. du Pont de Nemours & Co.

Example VI.—Bonadur Red B, an insolubilized azo dye available from Colway Colors. This pigment is a dye described in C.I. No. 15865 with hydrogen substituted for the potassium in the compound to insolubilize it.

Example VII.—Calcium Lithol Red, the calcium lake of 1-(2’-azonaphthalene-1’-sulfonic acid)-2-naphthol, C.I. No. 15630, available from Colway Colors.

Example VIII.—Indofast Double Scarlet Toner, a pyranthrone-type pigment, available from Harmon Colors. This pigment is a polynuclear aromatic having the following structure:

Example IX.—Quinol magenta RV-6903, a quinacridone-type pigment, available from Harmon Colors, having the following structure:

Example XI.—Indofast Red MV—6606, a thioindoxyl-type pigment, available from Harmon Colors, having the following structure: (dichlorothioindigo)

Example XII.—Vulcan Fast Red BBE Toner 35—2201, 3,3'-dimethoxy-4,4'-diphenyl-bis(1',-phenyl-3'-methyl-4'-azo-2'-pyrazolin-5'-one), C.I. No. 21200, available from Colway Colors.

Example XIII.—Pyrazolone Red B Toner, C.I. No. 21120, available from Colway Colors, having the following structure:

Example XIV.—Cyan Blue GTHF, the beta form of copper phthalocyanine, C.I. No. 74160, available from Colway Colors.

Example XV.—Cyan Blue XR, the alpha form of copper phthalocyanine, available from Colway Colors.

Example XVI.—Monolite Fast Blue GS, the alpha form of metal-free phthalocyanine, C.I. No. 74160, available from Arnold Hoffman Company.

Example XVII.—Monolite Fast Blue GS with about 3 mol percent 2,4,7-trinitro-9-fluorenone added to the suspension.

Example XVIII.—Monolite Fast Blue GS with about 2 mol percent benzonitrile added to the suspension.

Example XIX.—Monolite Fast Blue GS treated by milling in o-dichlorobenzene.

Example XX.—Methyl Violet, a photosensitivity molybdenum acid lake of 4-(N,N',N'-trimethylanilino)methylene-N,N'—dimethylaminol chloride, C.I. No. 42555, available from Colway Colors.

Example XXI.—Indofast Violet Lake, dichloro-9,18-isoviolanthrone, C.I. No. 60010, available from Harmon Colors.

Example XXII.—Diane Blue, 3,3'-methoxy-4,4'-diphenyl-bis(1'—azo-2'—hydroxy—3'—naphthylanilide), C.I. No. 21180, available from Harmon Colors.

Example XXIII.—A polychloro substituted copper phthalocyanine, C.I. No. 74260, available from Imperial Color and Chemical Company.

Example XXIV.—Indanthrene Brilliant Orange RK, 4,10-dibromo-6,12-anthraniline, C.I. No. 59300, available from General Dyestuffs.

Example XXV.—Algol Yellow GC, 1,2,5,6-dih(C,C'-diphenyl)-thiazole-anthraquinone, C.I. No. 67300, available from General Dyestuffs.

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**TABLE 1**

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**EXAMAPLES XXX—XXXV**

These examples compare image quality obtained with varying inter-electrode spacing. Each of these examples is carried out in an apparatus of the general type described in Example I—XXIX, above. For each example, a positive potential of about 2,000 volts is imposed on the core of the blocking electrode roller. The original used is
a black-and-white line copy transparency. In each example, the imaging suspension consist of about 8 parts by weight of particles of Monlile Fast Blue GS, alpha form metal-free phthalocyanine, available from the Arnold Hoffman Company, having an average particle diameter of less than 1 micron, dispersed in about 100 parts Solio Odorless Solvent 3440. The suspension layer coated on the imaging electrode before imaging has a thickness of about 2 mils greater than the interelectrode spacing. The results obtained with various interelectrode spacings are as follows:

Example XXX.—The inter-electrode gap is about 20 mils, so that the applied electric field is just under 100 volts per mil. The image produced is of very low quality with low density and very high background.

Example XXXI.—The inter-electrode spacing is about 10 mils, so that the applied electric field is just under 200 volts per mil. The image is of low quality with high background; image quality is only slightly greater than in Example XXX.

Example XXXII.—The inter-electrode spacing is about 5 mils, so that the applied electric field is just under 400 volts per mil. An image of satisfactory quality is obtained, with good density but high background.

Example XXXIII.—The inter-electrode spacing is about 1 mil, so that the applied electric field is just under 2,000 volts per mil. The resulting image is of excellent quality with high image density and low background.

Example XXXIV.—The inter-electrode spacing is about 0.5 mil, so that the applied electric field is just under 4,000 volts per mil. The resulting image is of excellent quality with excellent density and low background.

Example XXXV.—The inter-electrode spacing is about 0.2 mil. At this spacing, the roller is pressed very tightly against the imaging suspension. With the imaging suspension in place this is approximately the minimum spacing obtainable. At this spacing, the applied electric field is about 10,000 volts per mil. The resulting image is of excellent quality with excellent density and low background.

**EXAMPLES XXXVI—XLII**

Each of these examples is carried out in an apparatus of the general type described in Examples I—XXIX, above. These examples compare images obtained with varying potential applied to the suspension between the electrodes. In each of these examples, the polarity of the applied potential is positive. The original used is a black-and-white line copy transparency. A gap of about 1 mil is maintained between the electrodes throughout these examples. The electrically photosensitive particles consist of Algol Yellow GC, 1,2,5,6-dif(C,C'-diphenyl)-thiazole-anthraquinone, C.I. No. 67300, available from General Dyestuffs. About 8 parts by weight of this material having an average particle size of less than 1 micron is dispersed in about 100 parts Isopar G. A layer of this suspension having a thickness of about 3 mils is coated on the injecting electrode immediately before imaging. The results obtained with different potentials are as follows:

Example XXXVI.—The applied potential is about 50 volts, resulting in an electric field of just under 50 volts per mil across the imaging suspension. An image of very low quality with low density and a splotchy appearance results.

Example XXXVII.—The applied potential is about 100 volts, so that the electric field across the suspension is just under 100 volts per mil. The image resulting is of low quality with low density and is irregular in coverage.

Example XXXVIII.—The applied potential is about 300 volts so that the electric field applied is just under 300 volts per mil. An image of satisfactory quality is obtained with low density and some irregularity in density across the image.

Example XXXIX.—The potential applied is about 500 volts so that the electric field across the suspension is just under 500 volts per mil. An image of good quality results, with good density and uniformity.

Example XL.—The applied potential is about 1,000 volts so that the electric field across the suspension is just under 1,000 volts per mil. An image of excellent quality with good density and uniformity results.

Example XLI.—The applied potential is about 300 volts so that the electric field across the suspension is just under 300 volts per mil. An image of excellent quality with excellent density and uniformity results.

**EXAMPLES XLII—XLV**

Each of these examples is carried out in an apparatus of the general type illustrated in FIGURE I, as described in Examples I—XXIX, above. These examples are intended to illustrate the effect of varying particle size on image quality. The original image to be reproduced here is a black and white transparency containing high resolution line copy material. The inter-electrode gap is about 1 mil and a positive potential of about 2,000 volts is applied to the blocking electrode core. The photosensitive particles consist of Watchung Red B, a barium salt of 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphtholic acid, C.I. No. 15865, available from E. I. du Pont de Nemours & Co. About 8 parts by weight of this material in finely divided form is dispersed in about 100 parts Solio Odorless Solvent 3440. A layer of this suspension having a thickness of about 3 mils is coated onto the injecting electrode surface immediately before imaging. The quality of the images obtained with varying particle sizes is as follows:

Example XLII.—The particles have an average diameter of about 0.5 micron. The resulting image is of excellent quality with uniform coverage and high density.

Example XLIII.—The average particle size is about 1 micron. The resulting image is of good quality with high density and high resolution, the resolution being nearly as good as in Example XLII.

Example XLIV.—The average particle size is about 5 microns. The resulting image is of good quality with high density but noticeable fall off in image uniformity.

Example XLV.—The average particle size is about 20 microns. The image is of good quality with good density but very poor density uniformity across the image.

**EXAMPLES XLVI—L**

Each of these examples is carried out in an apparatus of the general type schematically illustrated in FIGURE I with the imaging mix coated on a NESA glass substrate through which exposure is made. These examples are intended to illustrate the effect of varying the concentration of photosensitive particles in the carrier liquid. For each example, a positive potential of about 2,000 volts is imposed on the core of the blocking electrode roller. The original used is a black-and-white line copy transparency. The suspension layer is coated onto the injecting electrode surface before imaging to a thickness of about 2 mils. The inter-electrode gap is about 0.8 mil. The imaging suspension consists of varying amounts of particles of the beta form of metal-free phthalocyanine having an average particle diameter of less than 1 micron, dispersed in Solio Odorless Solvent 3440. The results obtained with various concentrations of particles in carrier liquid are as follows:

Example XLVI.—About 0.5 part by weight of the photosensitive particles is dispersed in about 100 parts by weight carrier liquid. The image resulting is of excellent quality, with very low density and a streaky appearance.

Example XLVII.—About 2 parts by weight of the photosensitive particles are dispersed in about 100 parts carrier liquid. An image of good quality with good density results.

Example XLVIII.—About 5 parts by weight of the photosensitive particles are dispersed in about 100 parts of the carrier liquid. The image is of excellent quality, with
high density and excellent uniformity of density across the image. Example XLIX.—About 10 parts by weight of the photo-sensitive particles are dispersed in about 100 parts by weight of the carrier liquid. The image resulting is of good quality with good density across the image.

Example L.—About 3 parts by weight of the imaging particles are dispersed in about 100 parts by weight of about 0.2 parts of liquid. The resulting image is of good quality but density is irregular across the image giving a mottled appearance.

**EXAMPLE LI**

A solution is prepared by dissolving about 5 parts by weight Amberol ST—137—X, a non-reactive unmodified 100 percent phenol-formaldehyde resin, available from Rohm and Haas Company, in a solvent mixture consisting of about 25 parts acetone and about 20 parts toluene. To this solution is added about 1 part 2,4,7-trinitro-9-fluorenone or in about 50 parts of solution. Odorless Solvent is added. This solution is spray dried to form particles having an average diameter of about 1 micron by the process described, for example, in copending application Ser. No. 380,080, filed July 2, 1964. About 8 parts by weight of the resulting particles is dispersed in about 90 parts 95 percent isopropanol. The resulting dispersion is then spray coated onto the NESA glass substrate of a device of the sort schematically shown in FIGURE 1a, to a layer thickness of about 2 microns. A positive potential of about 5,000 volts is imposed on the core of the blocking electrode roller. An inter-electrode gap of about 0.05 mill is used. The resulting image is a black-and-white line copy transparency. The image resulting is of satisfactory quality, with satisfactory density but high background. It is apparent that these particles have low sensitivity.

**EXAMPLE LIIF**

About 10 parts of Bakelite Polysulphone P1700, available from the Union Carbide Corporation, is dissolved in about 200 parts dichloromethane. To this solution is added a solution of about 5 parts 2,4,7-trinitro-9-fluorenone in about 50 parts cyclohexanone. To the solution is then added about 0.3 part Rhodamine B, a green dye, 9-(x-carboxyphenyl)-6-(diethylamino)-3-xanthene-3-yldiene-diethyl chloride, available from E. I. du Pont de Nemours and Company. The solution is stirred to insure complete mixture of the ingredients. About 5 parts of water finally are added (having an average particle diameter of about 0.1 micron) is dispersed in this solution. This dispersion is then spray dried to form particles having an average diameter of about 2 microns. About 5 parts by weight of these particles is dispersed in about 100 parts decaene. This dispersion is then coated onto the NESA glass surface of an imaging device of the sort shown in FIGURE 1a to a layer thickness of about 2 mils. The inter-electrode gap is set at about 1 mil and a positive potential of about 10,000 volts is applied to the blocking electrode core. The original image is reproduced with a black and white transparency containing line copy images. The resulting image is of satisfactory quality with low density and moderate background. It is apparent that these particles have low sensitivity.

Although specific components and proportions have been described in the above examples, other materials, as listed above, may be used with similar results, where suitable. In addition, other materials may be added to the electrophotographic, to the imaging suspension, or to either electrode to synergize, enhance, or otherwise modify their properties. For example, the pigment composition of this invention may be dye-sensitized or electrically sensitized if desired, or may be mixed with other photosensitive materials, 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 photoelectrophoretic imaging comprising subjecting a layer of a suspension to an applied electric field between a pair of electrodes, at least one of which is partially transparent, said electric field having a field strength of at least about 300 volts per mil, said suspension comprising a plurality of finely divided particles in a carrier liquid, each of said particles comprising an electrically photosensitive pigment, said pigment being both the primary electrically photosensitive ingredient and the primary colorant for said particle, and substantially simultaneously exposing said suspension to an image through said transparent electrode with a source of electromagnetic radiation, whereby an image is formed.

2. The method of claim 1 wherein said suspension is brought into and out of an inter-electrode spacing of at least about 1 mil while said electric field application and said exposure continue.

3. The method of claim 1 wherein said electrodes are brought into and out of an inter-electrode spacing of at least about 0.2 mil while said electric field application and said exposure continue.

4. The method of claim 1 wherein said particles have an average size up to about 5 microns.

5. The method of claim 1 wherein said particles have an average size up to about 1 micron.

6. The method of claim 1 wherein said particles have a substantially insulating hydrocarbon liquid.

7. The method of claim 1 wherein at least one of said electrodes has a blocking structure.

8. The method of claim 1 wherein said electric field has a field strength of at least about 2,000 volts per mil.

9. The method of claim 1 wherein said particles have an average diameter of up to about 5 microns.

10. The method of claim 1 wherein said particles have an average diameter of up to about 1 micron.

11. The method of claim 1 wherein said electrodes are brought into and out of an inter-electrode spacing of at least about 1 mil while said electric field application and said exposure continue, and wherein said suspension is coated onto the surface of said electrodes to a thickness of from about 2 to 3 mils before imaging.

12. The method of claim 1 wherein at least one of said electrodes has a blocking structure.

13. The method of claim 1 wherein said electric field has a field strength of at least about 2,000 volts per mil.

14. The method of claim 1 wherein said particles have an average diameter of up to about 5 microns.

15. The method of claim 1 wherein said particles have an average diameter of up to about 1 micron.
18. The method of claim 17 wherein said electrodes are brought into and out of an inter-electrode spacing of up to about 1 mil while said electric field application and said exposure continue.

19. The method of claim 17 wherein said electrodes are brought into and out of an inter-electrode spacing of about 0.2 mils while said electric field application and said exposure continue.

20. The method of claim 17 wherein said particles have an average size up to about 5 microns.

21. The method of claim 17 wherein said particles have an average size of up to about 1 micron.

22. The method of claim 17 wherein said carrier liquid is a substantially insulating hydrocarbon liquid.

23. The method of claim 17 wherein from about 2 to about 10 parts by weight of said particles are dispersed in about 100 parts by weight of said carrier liquid.

24. The method of claim 17 wherein from about 5 to about 6 parts by weight of said particles are dispersed in about 100 parts by weight of said carrier liquid.

25. The method of claim 17 wherein a film-forming binder is dissolved in said carrier liquid and including the step of evaporating said carrier liquid from said image.

26. The method of claim 17 further including the step of overcoating the image formed on said electrode.

27. The method of claim 17 including the further step of transferring said image from at least one of said electrodes to the surface of a transfer member.

28. The method of claim 17 wherein at least one of said electrodes has a blocking surface.

29. The method of claim 17 wherein said electric field has a field strength of at least about 2,000 volts per mil.

30. The method of claim 17 wherein said particles have an average diameter of up to about 5 microns.

31. The method of claim 17 wherein said particles have an average diameter of up to about 1 micron.

32. The method of claim 17 wherein said electrodes are brought into and out of an inter-electrode spacing of about 1 mil while said electric field application and said exposure continue, and wherein said suspension is coated onto the surface of one of said electrodes to a thickness of from about 2 to 3 mils before imaging.

References Cited

UNITED STATES PATENTS

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<td>Moncrieff-Yates</td>
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<td>2,940,847</td>
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<td>3,058,914</td>
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<td>Metcalfe et al.</td>
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