

May 21, 1968

H. E. CLARK

3,384,566

METHOD OF PHOTOELECTROPHORETIC IMAGING

Filed July 21, 1967

2 Sheets-Sheet 1

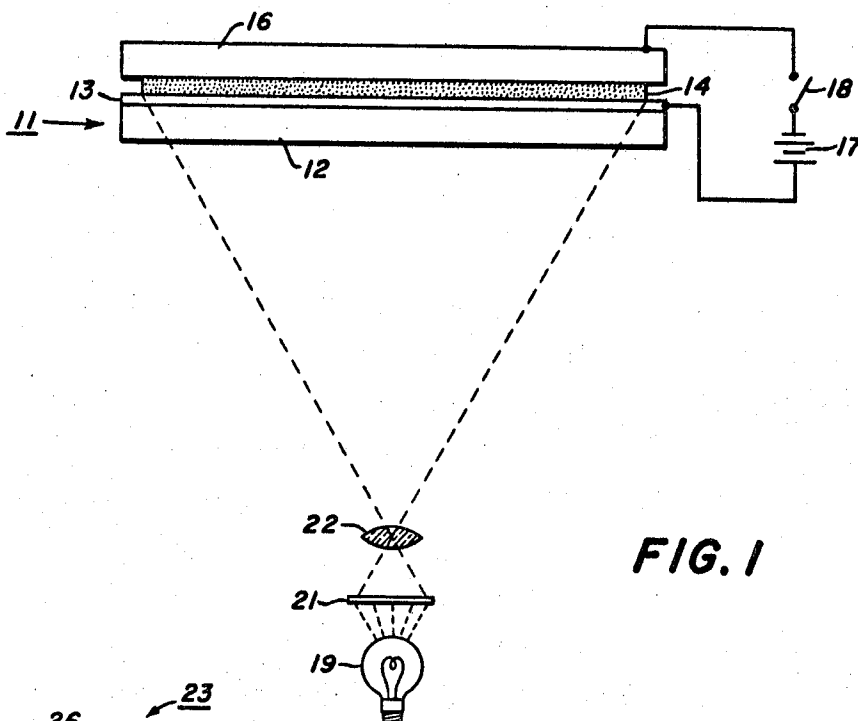


FIG. 1

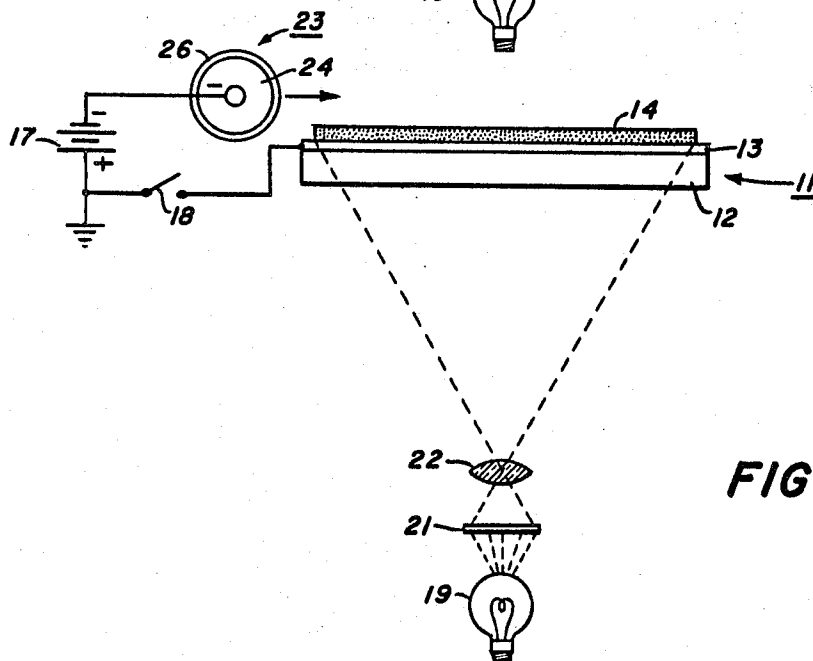


FIG. 1A

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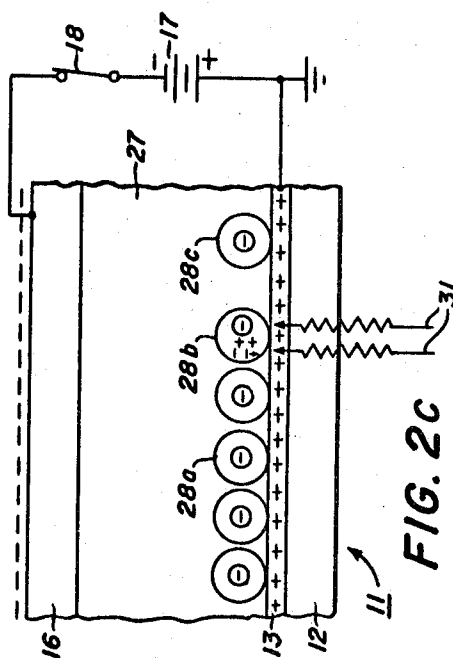
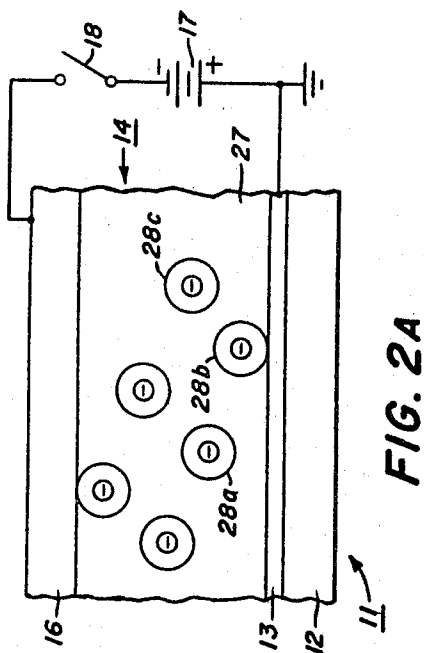
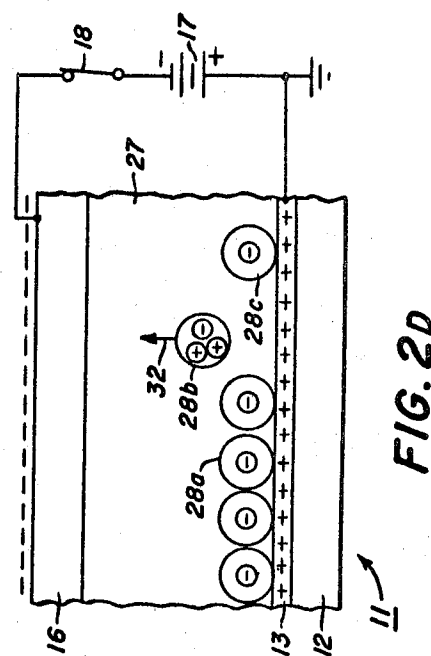
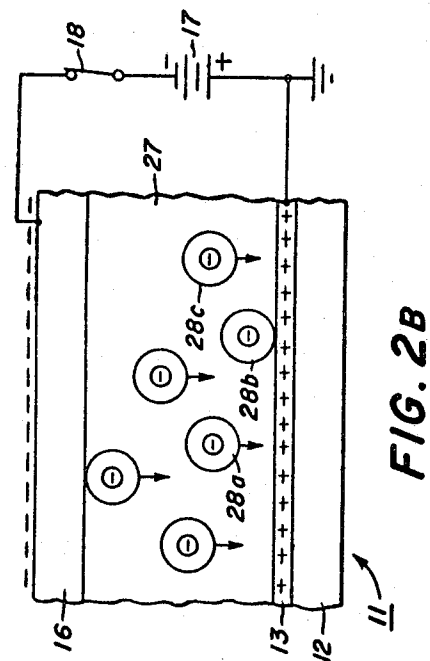
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METHOD OF PHOTOELECTROPHORETIC IMAGING

Filed July 21, 1967

2 Sheets-Sheet 2



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3,384,566 METHOD OF PHOTOELECTROPHORETIC IMAGING

Harold E. Clark, Penfield, N.Y., assignor to Xerox Corporation, Rochester, N.Y., a corporation of New York
Continuation-in-part of application Ser. No. 384,681,
July 23, 1964. This application July 21, 1967, Ser.
No. 655,023

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 photoelectrophoresis. 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 thermographic 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 aforementioned 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 believed to bear a charge when suspended in a substantially nonconductive liquid carrier are suspended in such a liquid, placed in an electrode 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 pigments 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

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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 so that when switch 18 is closed, an electric field is applied across the liquid suspension 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 blocking 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 fixed in place, as for example, by placing a lamination over its top surface or by virtue of a dissolved binder material in the carrier liquid such as paraffin wax or other suitable binders that come out of solution as the carrier liquid evaporates. About 3-6% by weight of paraffin binder in the carrier has been found to produce good results. The carrier liquid itself may be molten paraffin wax or other suitable binder in a liquid state which is self-fixing upon cooling and return to the solid state. In the alternative, the image remaining on the injecting electrode may be transferred to another surface and fixed thereon.

FIGURES 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 suspended particles 28 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. Particles 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 injection 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-

ticles 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 28b move up through the liquid carrier 27 from surface 13 towards electrode 16, 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 electrodes 11 and 16. These are that electrode 11 will preferably be capable of accepting injected electrons from bound particle 28b 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 28b at more than a very slow rate when it comes 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 particles at more than a very slow rate when they come into contact with the surface of this electrode. In this preferred embodiment, electrode 11 may be composed not only of conventional conductive materials such as tin oxide, copper, copper iodide, gold or the like but may also include many slightly conductive materials such as raw cellophane which are not ordinarily thought of as conductors but which are still capable of accepting injected charge carriers of the proper polarity under the influence of the applied field. Even highly insulating materials such as polytetrafluoroethylene may be placed over the surface of the "injecting" electrode and still be operative because charge which leaves the particles initially bound on this surface upon exposure to light can merely move out of the particles and remain on the insulating surface thereby allowing the exposed particles to migrate. However, the use of the more conductive materials is preferred because it allows for cleaner charge separation in that charge leaving the particles upon exposure can move into the underlying surface and away from the particle in which it originated. This also prevents possible charge buildup on the electrode which might tend to diminish the inter-electrode field. On the other hand, the preferred embodiment of the blocking electrode 16 is selected so as to prevent or greatly retard the injection of electrons (or holes, depending upon the initial polarity of charge on the particle) into particle 28b when it reaches the surface of this electrode. Accordingly, the surface of this electrode facing carrier liquid 27 in the preferred embodiment may be either an insulator or a semiconductor which will not allow for the passage of sufficient charge carriers under the influence of the applied field to discharge the particles finally bound to it thereby preventing particle oscillation in the system. Even if this blocking electrode will allow for the passage of some charge carriers through it to the particles, it will still be considered to come within the class of preferred materials if it does not allow for the passage of sufficient carriers to recharge the particle to the opposite polarity because even a discharged particle will tend to adhere to this blocking electrode by Van Der Waals forces. Here again, materials not coming within the preferred class may be employed but they tend to lead the particle oscillation in the system, resulting in lower image density, poorer image resolution, image reversal and similar deficiencies, with the degree of these deficiencies, in most instances depending upon how far the material employed deviates from the preferred class of materials in its electrical characteristics. Baryta paper and other suitable mate-

rials may be employed to surface the blocking electrode and may be wet on their back surfaces with tap water or coated on these back surfaces with electrically conductive materials. Baryta paper consists of a paper coated with barium sulfate suspended in a gelatin solution. The terms "blocking electrode" and "injecting electrode" should be understood and interpreted in this context throughout the specification and claims. As described in greater detail hereinafter, the system may be operated with suspensions of particles which initially take on a net positive charge, or a net negative charge, and even with systems where the particles in suspension apparently take on both polarities of charge.

Suitable substantially insulating carrier liquids for the system include decane, dodecane, N-tetradecane, molten paraffin, molten beeswax, Sohio Odorless Solvent 3440 (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). Any other suitable substantially insulating liquid may be used.

A wide range of voltages may be employed between the electrodes in this system. For good image resolution, high image density and low background, it is preferred that the potential applied be such as to create an electrical field of at least about 300 volts per mil across the imaging suspension. The applied potential necessary to attain this field strength 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 core 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 imaging liquid 14 and may be virtually any color in which it is desired to produce the final image such 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 wavelengths in the visible spectrum, thus allowing for color separation. It should be noted, however, that this separation of spectral responses of differently colored included particles 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, which when combined will produce a black image. In this latter instance, considerable overlap and even coincidence of the

spectral response curves of the different pigments may be tolerated and may even be preferred so that all of the pigments employed in the system will respond in a substantially similar way to generally available light sources which are not uniformly panchromatic in their light output. Clearly, if a white light source is used, this overlap is not a requirement.

Any suitable photosensitive particle or mixtures of such particles may be used in carrying out the invention, regardless of whether the particular particle selected is organic, inorganic and is made up of one or more components in solid solution or dispersed one in the other or whether the particles are made up of multiple layers of different materials. Typical organic pigments include: quinacridones such as: 2,9-dimethyl quinacridone, 4,11-dimethyl quinacridone, 3,10-dichloro-6,13-dihydro-quinacridone, 2,9-dimethoxy-6,13-dihydro-quinacridone, 2,4,9,11-tetrachloro-quinacridone, and solid solutions of quinacridones and other compositions as described in U.S. Patent 3,160,510; carboxamides such as: N-2''-pyridyl-8,13-dioxodinaaphtho-(1,2-2',3') furan-6-carboxamide, N-2''-(1'',3''-diazyl)-8,13-dioxodinaaphtho-(1,2-2',3') furan-6-carboxamide, N-2''-(1'',3'',5''-triazyl)-8,13-dioxodinaaphtho-(1,2-2',3') furan-6-carboxamide, anthra-(2,1,β)-naphtho-(2,3-d)-furan-9,14-dione-7-(2'-methylphenyl)carboxamide; carboxanilides such as: 8,13-dioxodinaaphtho-(1,2-2',3')-furan-6-carbox-p-methoxy-anilide, 8,13-dioxodinaaphtho-(1,2-2',3')-furan-6-carbox-p-methylanilide, 8,13-dioxodinaaphtho-(1,2-2',3')-furan-6-carbox-m-chloroanilide, 8,13-dioxodinaaphtho-(1,2-2',3')-furan-6-carbox-p-cyanoanilide; triazines such as: 2,4-diaminotriazine, 2,4-di-(1'-anthraquinonyl-amino)-6-(1''-pyrenyl)-triazine, 2,4-di-(1'-anthraquinonyl-amino-6-(1''-naphthyl)-triazine, 2,4-di-(1'-naphthyl-amino)-6-(1'-perylene)-triazine, 2,4,6-tri-(1',1'',1'''-pyrenyl)-triazine; benzopyrrocolines such as: 2,3-phthaloyl-7,8-benzopyrrocoline, 1-cyano-2,3-phthaloyl-7,8-benzopyrrocoline, 1-cyano-2,3-phthaloyl-5-nitro-7,8-benzopyrrocoline, 1-cyano-2,3-phthaloyl-5-acetamido-7,8-benzopyrrocoline; anthraquinones such as: 1,5-bis-(beta-phenylethylamino) anthraquinone, 1,5-bis-(3'-methoxypropylamino) anthraquinone, 1,5-bis (benzylamino) anthraquinone, 1,5-bis (phenylbutylamino) anthraquinone, 1,2,5,6-di(C,C'-diphenyl)-thiazole-anthraquinone, 4-(2'-hydroxyphenyl-methoxy-amino) anthraquinone; azo compounds such as: 2,4,6-tris (N-ethyl-N-hydroxy-ethyl-p-aminophenylazo) phloroglucinol, 1,3,5,7-tetrahydroxy-2,4,6,8-tetra (N-methyl-N-hydroxyethyl-p-amino-phenylazo) naphthalene, 1,3,5-trihydroxy-2,4,6-tri (3'-nitro-N-methyl-N-hydroxymethyl-4'-aminophenylazo) benzene, 3-methyl-1-phenyl-4-(3'-pyrenylazo)-2-pyrazolin-5-one, 1-(3'-pyrenylazo)-2-hydroxy-3-naphthanilide, 1-(3'-pyrenylazo)-2-naphthol, 1-(3'-pyrenylazo)-2-hydroxypyrene, 1-(3'-pyrenylazo)-2-hydroxy-3-methyl-xanthene, 2,4,6-tris (3'-pyrenylazo) phloroglucinol, 2,4,6-tris (1'-phenanthrenylazo) phloroglucinol, 1-(2'-methoxy-5'-nitro-phenylazo)-2-hydroxy-3''-nitro-3-naphthanilide; salts and lakes of compounds derived from 9-phenylxanthene, such as: phosphotungstomolybdic lake of 3,6-bis (ethylamino)-9,2'-carboxyphenyl xanthenonium chloride, barium salt of 3-2'-toluidine amino-6-2''-methyl-4''-sulphophenyl-amino-9-2'''-carboxyphenyl xanthene; phosphomolybdic lake of 3,6-bis (ethylamino)-2,7-dimethyl-9-2'-carbethoxyphenyl xanthenonium chloride; dioxazines such as: 2,9-dibenzoyl-6,13-dichloro-triphenodioxazine, 2,9-diacetyl-6,13-dichloro-triphenodioxazine, 3,10-dibenzoylamino-2,9-diisopropoxy-6,13-dichloro-triphenodioxazine, 2,9-difuroyl-6,13-dichloro-triphenodioxazine; lakes of fluorescein dyes, such as: lead lake of 2,7-dinitro-4,5-dibromo fluorescein, lead lake of 2,4,5,7-tetrabromo fluorescein, aluminum lake of 2,4,5,7-tetrabromo-10,11,12,13-tetrachloro fluorescein; bisazo compositions such as: N,N'-[1-(1'-naphthylazo)-2-hydroxy-8-naphthyl] adipdiamide, N,N'-di-1-(1'-naphthylazo)-2-hydroxy-8-naphthyl succindiamide, bis-4,4'-(2''-hydroxy-8''-N,N'-diterephthalamide-1-naphthylazo)biphenyl, 3,3'-methoxy-4,4'-diphenyl-bis(1''-azo-2''-hydroxy-3''-naphthanilide); pyrenes such as: 1,3,6,8-tetracyanopyrene, 1,3-dicyano-6,8-dibromopyrene, 1,3,6,8-tetraaminopyrene, 1-cyano-6-nitropyrene; phthalocyanines such as: beta-form metal-free phthalocyanine, copper phthalocyanine, tetrachloro phthalocyanine, the x-form of metal-free phthalocyanine as described in copending application Ser. No. 505,723, filed Oct. 29, 1965; metal salts and lakes of azo dyes, such as: calcium lake of 6-bromo-1(1'-sulfo-2-naphthylazo)-2-naphthol, barium salt of 6-cyano-1(1'-sulfo-2-naphthylazo)-2-naphthol, calcium lake of 1-(2'-azonaphthaliene-1'-sulfonic acid)-2-naphthol, calcium lake of 1-(4'-ethyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid; and mixtures thereof.

Typical inorganic compositions include cadmium sulfide, cadmium sulfoselenide, zinc oxide, zinc sulfide, sulphur selenium, mercuric sulfide, lead oxide, lead sulfide, cadmium selenide titanium dioxide, indium trioxide and the like. In addition to the aforementioned organic pigments other organic materials which may be employed in the particles include polyvinylcarbazole;

2,4-bis(4,4'-diethyl-aminophenyl)-1,3,4-oxidiazole; N-isopropylcarbazole; polyvinylanthracene; triphenylpyrrol;

4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinethione; 4,5-bis-(4'-amino-phenyl)-imidazolidinone; 1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8); 3,4-di-(4'-methoxyphenyl)-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8); 3,4-di-(4'-phenoxy-phenyl)-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8); 3,4,7,8-tetramethoxy-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8);

2-mercapto-benzthiazole; 2-phenyl-4-alpha-naphthylidene-oxazolone; 2-phenyl-4-diphenylidene-oxazolone; 2-phenyl-4-p-methoxybenzylidene-oxazolone; 6-hydroxy-2-phenyl(p-dimethyl-amino phenyl)-benzofurane; 6-hydroxy-2,3-di(p-methoxyphenyl)-benzofurane; 2,3,5,6-tetra-(p-methoxyphenyl)-fuoro-(3,2f)-benzofurane; 4-dimethylamino-benzylidenebenzhydrazide; 4-dimethyl-aminobenzylideneisonicotinic acid hydrazide; turfurylidene-(2)-4'-dimethylamino-benzhydrazide; 5-benzilidene-amino-acenaphthene-3-benzylidene-amino-carbazole;

(4-N,N-dimethylamino-benzylidene)-p-N,N-dimethyl-aminoaniline; (2-nitro-benzylidene)-p-bromo-aniline; N,N-dimethyl-N'-(2-nitro-4-cyano-benzylidene)-p-phenylene-diamine; 2,4-diphenyl-quinazoline; 2-(4'-amino-phenyl)-4-phenyl-quinazoline; 2-phenyl-4-(4'-dimethyl-amino-phenyl)-7-methoxy-quinazoline;

1,3-diphenyl-tetrahydroimidazole; 1,3-di-(4'-chlorophenyl)-tetra-hydroimidazole; 1,3-diphenyl-2-4'-dimethyl aminophenyl)-tetrahydroimidazole; 1,3-di-(p-tolyl)-2-[quinolyl-(2')] -tetrahydroimidazole; 3-(4'-di-methylamino-phenyl)-5-(4''-methoxy-phenyl)-6-phenyl-1,2,4-triazine; 3-pyridil-(4')-5-(4'-dimethylaminophenyl)-6-phenyl-1,2,4-triazine;

3-(4'-amino-phenyl)-5,6-di-phenyl-1,2,4-triazine; 2,5-bis[4'-amino-phenyl-(1')]-1,2,3-triazole; 2,5-bis[4'-(N-ethyl-N-acetyl-amino)-phenyl-(1')]-1,3,4-triazole;

1,5-diphenyl-3-methyl-pyrazoline;

1,3,4,5-tetraphenyl-pyrazoline;

1-phenyl-3-(p-methoxy styryl)-5-(p-methoxy-phenyl)-pyrazoline;
 1-methyl-2-(3',4'-dihydroxy-methylene-phenyl)-benzimidazole;
 2-(4'-dimethylaminophenyl)-benzoxazole;
 2-(4'-methoxyphenyl)-benzthiazole;
 2,5-bis[p-amino-phenyl-(1)]-1,3,4-oxiadiazole;
 4,5-diphenyl-imidazolone;
 3-amino-carbazole;

copolymers and 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, phenoxies, 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; picric acid; 1,3,5-trinitro benzene; chloranil; 2,5-dichlorobenzoquinone; 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, strontium bromide, chromic bromide, arsenic triiodide, magnesium bromide, stannous chloride etc.; boron halides, such as boron trifluorides; ketones such as benzophenone and anisil, mineral acids such as sulfuric acid; organic carboxylic acids such as acetic acid and maleic acid, succinic acid, citroconic acid, sulphonic acid, such as 4-toluene sulphonic acid and mixtures thereof. In addition 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 thermoplastic or thermosetting resins, copolymers of photosensitive pigments and organic monomers, multilayers of particles 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 fusable 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 overlayer of another photosensitive material to achieve broadened spectral response. Other photosensitive structures include solutions, dispersions, or copolymers of one photosensitive material in another with or without other photosensitively inert materials. While the above structural and compositional variations are useful, it is preferred that each particle be primarily composed of an electrically photosensitive pigment, 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 sensitivity 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 reproduce 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 than 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 having 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 this charge with respect to that of the electrodes. It is not necessary that the particles take on only one polarity of charge but instead the particles may be attracted to both electrodes. Some of the particles in the suspension initially move towards the "injecting" electrode while others move towards 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 effect of imagewise, exposure-induced migration is superimposed 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 imagewise 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 potential 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 concentration so that the system is still capable of producing intense images. It also has been found that with some suspensions 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 invention may be used in conventional dry modes of operation, it is believed that a different type of photoresponsive mechanism is involved because it has generally been found that 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 systems Van der Waals forces have a serious detrimental effect 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 5 mol percent) of electron donors or acceptors to the suspensions with the choice depending upon whether the particles attracted to the "injecting" electrode are positive or negative respectively has imparted significant increases in system photosensitivity as described in the examples. 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 as by spraying a binder on it, laminating an overlay on it or by including a binder in solution in the liquid suspending medium. In most instances, however, it will be found preferable 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 cellophane tape or preferably, by electrostatic field transfer. Electrostatic transfer may, for example, be carried out by carrying 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 potential opposite in polarity to that of the first electrode. If the second electrode roller is covered with a baryta

paper sleeve, this paper sleeve will pick up the complete image as the electrode rolls over it. For further details on this transfer system, see compending application Ser. No. 542,050, filed Apr. 12, 1966.

Although various electrode spacings may be employed, spacings of less than 1 mil and extending down even to the point where the electrodes are pressed together as in the case of the roller electrode of FIGURE 1a constitute a particularly preferred form of the invention in that they produce better image density and background than is produced with wider spacings. Wider spacings tend to result in very high background deposition. Optimum density and background are generally obtained with an inter-electrode spacing of about 0.2 mils (where the electrodes are pressed together).

Any suitable proportion of electrically photosensitive particles to carrier liquid may be used. It is preferred that from about 2 to about 10 weight percent particles be used for good balance between high image density and low background, consistent with particle economy. Less than 2 wt. percent particles tends to cause streaky images, while over 10 wt. percent particles tends to cause mottling in the image. Optimum image quality has been obtained with from about 5 to 6 weight percent particles.

The layer of the imaging suspension may be coated onto either electrode before imaging. Generally, the layer should have a thickness about 2 mils greater than the inter-electrode spacing to insure that both electrodes uniformly contact the suspension. Still greater relative layer thicknesses may be used, since the excess is merely squeezed out as the electrodes are brought into place. However, this excess is not needed for imaging and is uneconomical. Where the inter-electrode spacing is up to 1 mil, optimum results are obtained with a suspension layer thickness of 0.5 to 3 mils.

Description of preferred embodiments

The following illustrative examples are given to enable those skilled in the art to more clearly understand and practice the invention. Parts and percentages are by weight unless otherwise indicated. These examples may be considered to illustrate preferred embodiments of the present invention.

EXAMPLES I-XXIX

Each of these examples is carried out in an apparatus of the general type schematically illustrated in FIGURE 1a with the imaging mix 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 1.5 centimeters per second. The plate employed is roughly 3 inches square and is exposed with a light intensity of about 1800 foot-candles. About 7 percent by weight of the indicated finely divided photosensitive material in each example is suspended in Sohio Odorless Solvent 3440. During imaging, unless otherwise indicated, a positive potential of about 2500 volts is imposed on the core of the roller. The gap between the baryta paper surface and the NESA glass surface is about 1 ml. With all pigments which are received commercially with a relatively large particle size, the particles are ground in a ball mill for about 48 hours to reduce their size to an average diameter of less than 1 micron. Exposure is made with a 3200° K. lamp through a 0.30 neutral density step wedge filter to measure the sensitivity of the suspension to white light and then Wratten filters 29, 61 and 47b are individually superimposed over the light source in separate runs to measure the sensitivity of the suspension to red, green, and blue light, respectively. The relative sensitivity response figures obtained for the suspension are tabulated in Table I below. The sensitivity figures are derived from the number of steps step wedge filter which are discernible in the images

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 I.—Locarno Red X-1686, 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid) - 2 - hydroxy-3-naphthoic acid, C.I. No. 15865, available from American Cyanamid;

Example II.—Watchung Red B, a barium salt of 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, C.I. No. 15865, available from E. I. du Pont de Nemours & Co.;

Example III.—Permagen Red L toner 51-500, 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, C.I. No. 15865, available from Collway Colors;

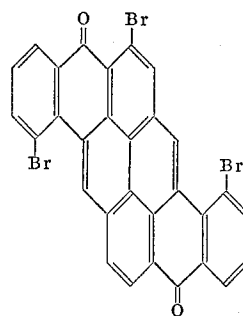
Example IV.—Naphthol Red B, 1-(2'-methoxy-5'-nitrophenylazo)-2-hydroxy-3''-nitro-3-naphthanilide, C.I. No. 12355, available from Collway Colors;

Example V.—Duol Carmen, the calcium lake of 1-(4'-methylazobenzene-2'-sulfonic acid) - 2-hydroxy-3-naphthoic acid, C.I. No. 15850, available from E. I. du Pont de Nemours & Co.;

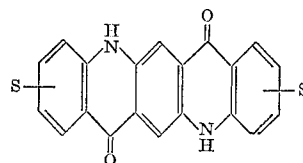
Example VI.—Bonadur Red B, an insolubilized azo dye available from Collway Colors. This pigment is a dye described in C.I. No. 15865 with hydrogen substituted for the sodium in the compound to insolubilize it.

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



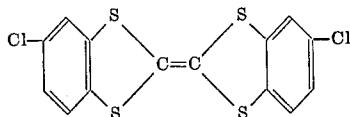
Example IX.—Quindo magenta RV-6803, a quinacridone-type pigment, available from Harmon Colors, having the following structure:



Example X.—Indofast Brilliant Scarlet Toner, 3,4,9,10-bis[N,N'-(p-methoxyphenyl)-imido]-perylene, C.I. No. 71140, available from Harmon Colors.

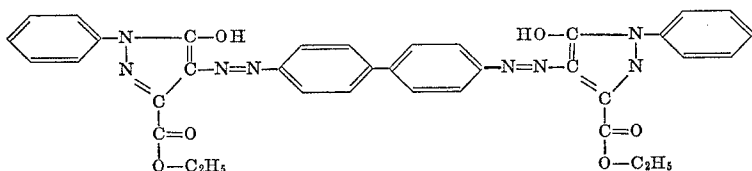
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Example XI.—Indofast Red MV-6606, a thioindoxyle-type pigment, available from Harmon Colors, having the following structure: (dichlorothioindigo)



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

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



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

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

Example XVI.—Monolite Fast Blue GS, the alpha form of metal-free phthalocyanine, C.I. 74100, 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 phosphotungstomolybdic acid lake of 4-(N,N',N'-trimethylanilino)methylene-N'',N''-dimethylanilinium chloride, C.I. No. 42535, available from Collway 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''-naphthanilide), 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-anthanthrone, C.I. No. 59300, available from General Dyestuffs.

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

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Example XXVI.—Algol Yellow GC, with the addition of about 2 mol percent 2,4,7-trinitro-9-fluorenone to the suspension.

Example XXVII.—Indofast Yellow Toner, flavanthrone, C.I. No. 70600, available from Harmon Colors.

Example XXVIII.—Indofast Orange Toner, a benzimidazole-type pigment, C.I. No. 71105, available from Harmon Colors.

Example XXIX.—Light Cadmium Orange Concentrate, a cadmium selenide pigment, C.I. No. 77196, available from Imperial Color and Chemical Company.

The relative spectral sensitivity of the above listed materials and the sign of the potential applied to the blocking electrode core are tabulated in Table 1 below.

TABLE 1

Example	Roller Electrode Polarity	Blue	Green	Red	White
I.....	(Positive.....	2	8	0	32
II.....	(Negative.....	2	8	0	32
III.....	(Positive.....	1	4	0	32
IV.....	(Positive.....	8	32	0	64
V.....	(Negative.....	8	32	0	64
VI.....	(Positive.....	1	4	0	16
VII.....	(do.....	4	16	1	64
VIII.....	(do.....	2	8	2	64
IX.....	(do.....	1	4	0	16
X.....	(do.....	4	8	0	32
XI.....	(do.....	2	16	0	128
XII.....	(do.....	32	64	0	128
XIII.....	(do.....	2	8	0	32
XIV.....	(Positive.....	16	32	0	64
XV.....	(Negative.....	8	12	0	32
XVI.....	(Positive.....	0	2	0	4
XVII.....	(Negative.....	1	4	0	16
XVIII.....	(Positive.....	1	1	16	32
XIX.....	(do.....	1	4	16	32
XX.....	(do.....	1	8	32	64
XXI.....	(do.....	2	16	64	128
XXII.....	(do.....	4	32	128	256
XXIII.....	(do.....	1	4	32	64
XXIV.....	(do.....	0	1	1	8
XXV.....	(do.....	0	8	0	32
XXVI.....	(do.....	0	1	8	16
XXVII.....	(do.....	0	0	16	32
XXVIII.....	(do.....	4	16	0	32
XXIX.....	(Negative.....	2	0	0	8
XXX.....	(Positive.....	32	8	0	128
XXXI.....	(do.....	16	4	0	64
XXXII.....	(do.....	0	8	16	32
XXXIII.....	(do.....	0	8	20	160
XXXIV.....	(Negative.....	80	0		

EXAMPLES 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 Monlite 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 Sohio Odorless Solvent 3440. The suspension layer coated on the injecting electrode before imaging has a thickness 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 electric field applied 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-XLI

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-di(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 3,000 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 1a and 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-naphthoic 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 Sohio 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 high 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 1a 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 Sohio 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 are dispersed in about 100 parts by weight carrier liquid. The resulting image is of low 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 the carrier 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. The mixture is stirred until solution of the materials is complete. 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 100 parts Sohio Odorless Solvent 3440. This dispersion is 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 3,000 volts is imposed on the core of the blocking electrode roller. An inter-electrode gap of about 0.5 mil is used. The original used 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 LII

About 10 parts of Bakelite Polysulfone P1700, available from the Union Carbide Corporation, is dissolved in about 200 parts dichloromethane. To this solution is added a solution of about 3 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-(o-carboxyphenyl)-6-(diethylamino)-3-xanthene-3-ylidene-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 very finely divided zinc oxide (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 decane. 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 to be reproduced here is 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 electrically photosensitive particles, to the imaging suspension, or to either electrode to synergize, enhance, or otherwise modify their properties. For example, the pigment compositions 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 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.

3. The method of claim 1 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.

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 of up to about 1 micron.

6. The method of claim 1 wherein said carrier liquid is a substantially insulating hydrocarbon liquid.

7. The method of claim 1 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.

8. The method of claim 1 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.

9. The method of claim 1 wherein a film-forming binder is dissolved in said carrier liquid and including the step of evaporating said carrier liquid from said image.

10. The method of claim 1 further including the step of overcoating the image formed on said electrode.

11. The method of claim 1 including the further step of transferring said image from at least one of said electrodes to the surface of a transfer member.

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

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.

16. The method of claim 1 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, 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.

17. The method of photoelectrophoretic imaging comprising applying a layer of a suspension onto an electrode, 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, bringing a second electrode into an inter-electrode spacing of up to about 1 mil, at least one of said electrodes being partially transparent, applying an electric field across said suspension between said electrodes, said potential being at least about 300 volts, and substantially simultaneously exposing said suspension to an image through said transparent electrode with a source of activating electromagnetic radiation, whereby an image is formed.

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 up to 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.

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