

[54] **PHOTOELECTROPHORETIC IMAGING APPARATUS**

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Related U.S. Application Data

[60] Division of Ser. No. 144,215, May 17, 1971, which is a continuation of Ser. No. 707,871, Feb. 23, 1968, abandoned.

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[58] Field of Search 355/3 P, 4, 10; 118/637, 118/DIG. 23; 117/37 LE; 96/1.3, 1.2, 1 LY; 204/181 PE

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Primary Examiner—Richard L. Moses

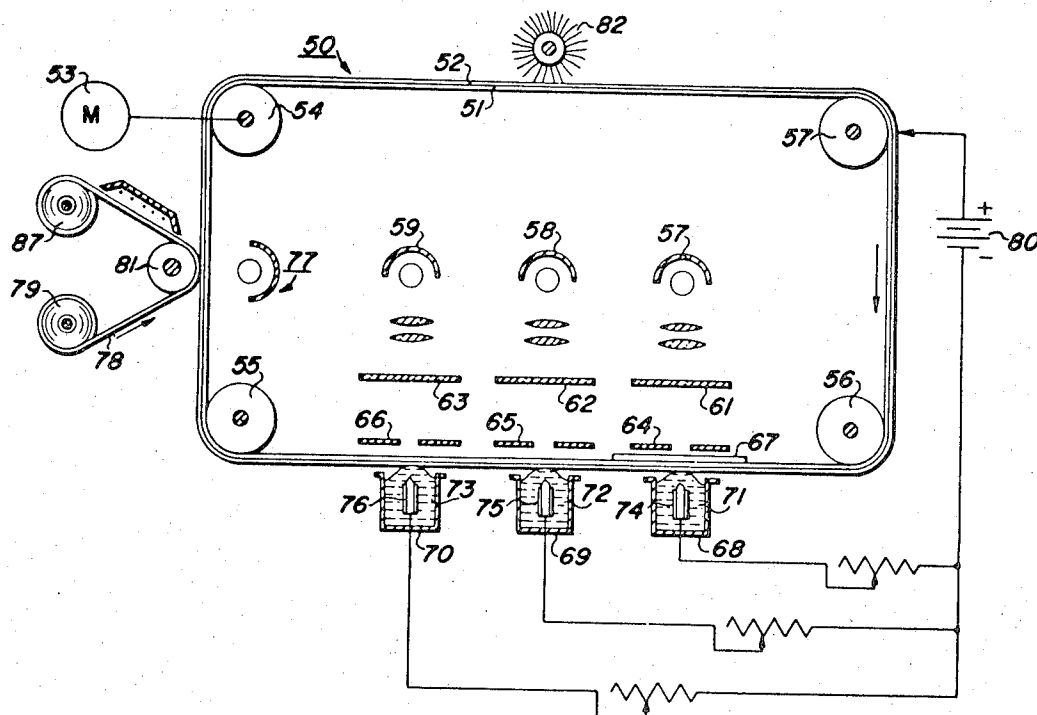
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[57]

ABSTRACT

A device for photoelectrophoretic imaging wherein a localized electric field is developed by a transparent electrode-coronode system, in conjunction with an imaging suspension. As a result of a non-homogeneous electric field developed in the imaging suspension, upon exposure selectively to an electromagnetic radiation source through the transparent electrode, an image is formed in the non-illuminated areas on the surface of the transparent electrode.

2 Claims, 2 Drawing Figures



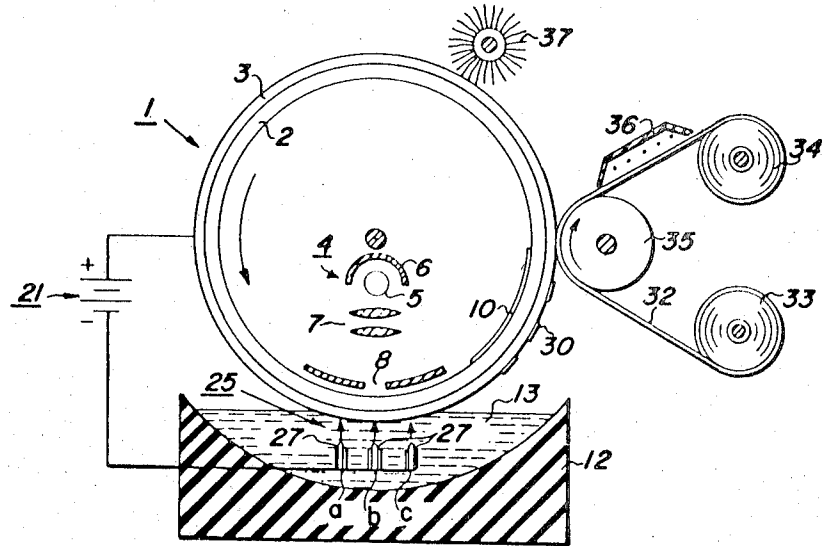


FIG. 1

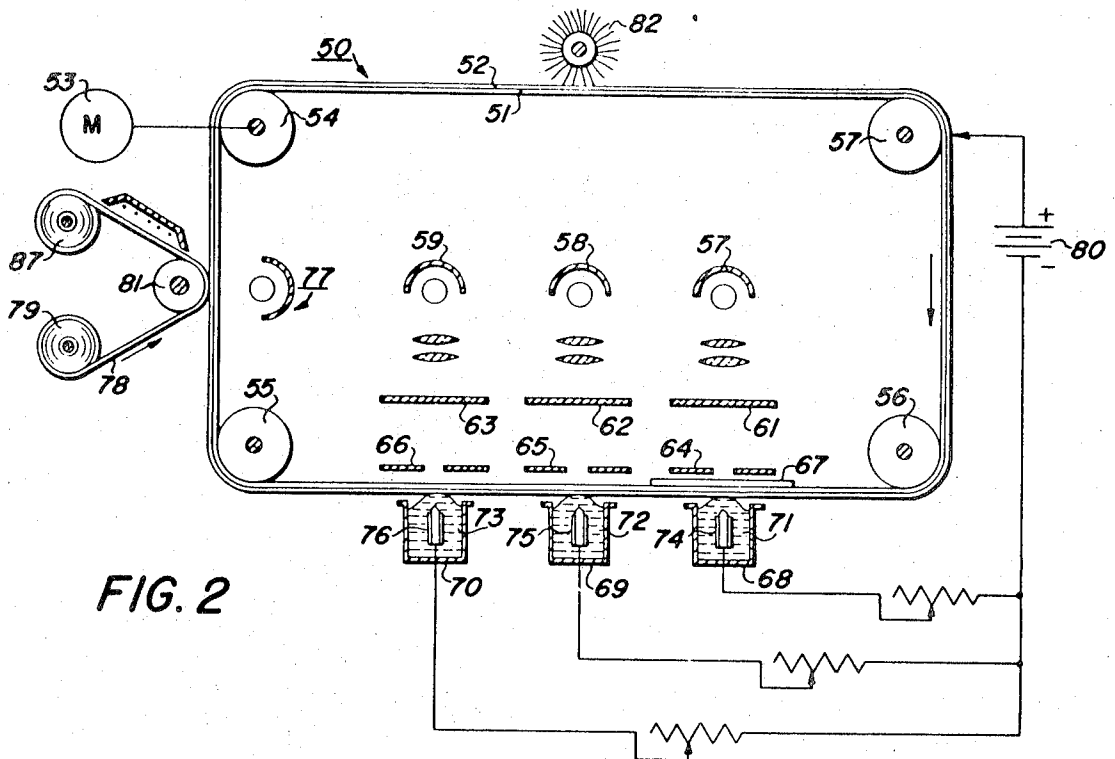


FIG. 2

PHOTOELECTROPHORETIC IMAGING APPARATUS

CROSS-REFERENCE TO RELATED CASES

This is a divisional application of copending application Ser. No. 144,215, filed May 17, 1971, which is a continuation application of prior copending application Ser. No. 707,871, filed Feb. 23, 1968, and now abandoned.

This invention relates to an imaging system and, more specifically, to an electrophoretic imaging system.

In photoelectrophoretic imaging colored photosensitive particles are suspended in an insulating carrier liquid. This suspension is then placed between a pair of electrodes, subjected to a potential difference and exposed to an image to be reproduced. Ordinarily, in carrying out the process, the imaging suspension is placed on a transparent electrically conductive plate in the form of a thin film and exposure is made through the bottom of this plate while a second generally cylindrical shaped electrode is rolled over the top of the suspension. The particles are believed to bear an initial charge when suspended in the liquid carrier which causes them to be attracted to the transparent base electrode and, upon exposure, to change polarity by exchanging charge with this base electrode so that the exposed particles then migrate away from the base electrode to the roller electrode thereby forming images on both electrodes, by particle subtraction, each image being complimentary to the other. The process may be used to produce both polychromatic and monochromatic images. In the latter instance a single color photoresponsive particle may be used in the suspension or a number of differently colored photoresponsive particles may be used in the suspension all of which will respond to the same wavelength of light exposure. An extensive and detailed description of the photoelectrophoretic imaging technique, as described above, is found in copending U.S. Pat. applications Ser. Nos. 384,737 now Pat. No. 3,384,565; 384,681; now abandoned and 384,680, now abandoned filed Jan. 23, 1964, having a common assignee.

Although it has been found that good quality images can be produced with migration of the particles depending on the conditions of exposure, generally in all instances images will be formed on both of the electrodes in the system. Inasmuch as only one of the images formed is the desired end product, the imaging suspension is unnecessarily depleted of the photosensitive pigment. It is, therefore, necessary to repeatedly replenish the supply of the imaging suspension, thus substantially effecting the efficiency of the system.

It is, therefore, an object of this invention to provide an imaging system which will overcome the above noted disadvantages.

It is a further object of this invention to provide a novel imaging system capable of producing high contrast, low background images.

Another object of this invention is to provide an imaging system capable of producing a single high contrast image.

It is still a further object of this invention to provide a novel electrophoretic imaging system.

Yet, still a further object of this invention is to provide a novel electrophoretic imaging apparatus.

Yet, still another object of this invention is to provide an electrophoretic imaging system which utilizes the effect of a non-uniform electric field in image development.

5 A further object of this invention is to provide a novel monochromatic and polychromatic imaging system.

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing a suspension of photoelectrophoretic imaging particles in an insulating carrier liquid. The process comprises the development of a localized electric field by an electrode-coronode system in conjunction with the imaging suspension. Generally speaking, the imaging suspension is contacted with the surface of a transparent electrically conductive imaging electrode such as NESA glass, tin oxide coated glass, and at least one coronode is immersed in the imaging suspension. An electric field is established by way of the electrode system in the imaging suspension while the latter is simultaneously exposed to a reproducible image through the transparent electrode. As a result of the non-uniform electric field present in the system, the photoconductive pigment particles present in the suspension will migrate towards the transparent electrode. In the illuminated areas the photosensitive particles are thought to exchange charge with the transparent electrode and are repelled from the electrode surface. Pigment deposition, nevertheless, is realized in the non-illuminated areas on the transparent electrode in imagewise configuration. The process of the present invention may be used to produce both polychromatic images by blending the necessary photoresponsive color particles and monochromatic images requiring one such photoreponsive particle.

15 In an alternate embodiment of the present invention it has been determined that as a result of the presence of at least one immersed coronode in the liquid imaging dispersion or suspension, it is now possible to regulate the size of the development zone, that is, the amount of developer which will contact the member upon which the image is to be formed for a particular pass. Depending upon the magnitude of the voltage applied, and the location of the coronode within the developer, the surface of the liquid developer may be deformed in such a manner so as to selectively contact the surface of the image bearing member. Therefore, it is now possible to regulate the density of the images produced. In addition, adapting this latter process to a polychromatic imaging system, it is also possible to produce a multicolor print in a stepwise mode by selective displacement of liquid developer containing the proper color pigment in a manner which eliminates conventional registration problems and the need for blending the various pigment mixes in one precarious suspension. By utilizing the proper filter systems in conjunction with the corresponding color pigment dispersed in a liquid carrier, as more fully described hereafter, it is now possible to directly produce color prints in a stepwise process having a built in registration system.

20 It has been determined in the course of the present invention that the migration of polarizable developer particles in an insulating liquid may be controlled and directed by the strategic placement of a coronode system providing a point source of electrical charge within the liquid imaging dispersion. At least one coronode is located with respect to an imaging electrode such that a uniform current is provided within the imaging sus-

pension. A non-uniform electric field is established within the region where ionization of the coronode takes place thus directing the flow of the now charged pigment particles away from the respective coronode and towards the imaging electrode. The resulting polarity of the field generally makes no difference upon the flow of the developer particles. The determining factor controlling the developer particle migration is the field strength established between the respective electrodes. When the expression point source is used in the course of the present invention it is intended to mean a localized source of energy such as a needle, wire, thin knife-like edge or other similar device.

The invention is further illustrated in the accompanying drawings in which:

FIG. 1 represents a continuous monochromatic imaging system;

FIG. 2 represents a polychromatic imaging system illustrating selective developer application.

Referring now to FIG. 1 there is seen a rotary transparent electrode 1 in the form of a drum which in this instance is made up of an optically transparent Mylar (polyethylene terephthalate) substrate 2 carrying on its outer surface a thin optically transparent conductive layer of aluminum 3. This rotary electrode may be referred to as the imaging electrode. Within the drum is an exposure station 4 comprising a light source 5 and shield 6 with a corresponding lense mechanism 7 so as to effectively focus the light of the exposure station at slit 8. The transparency to be printed, in one embodiment of the invention, may be fastened to the inner surface of the imaging electrode 1 as is illustrated by the original 10.

Positioned beneath the imaging electrode 1 is a container 12 for the electrophoretic imaging suspension 13. A high voltage source 21 connects the conductive layer 3 of the imaging electrode 1 to a coronode system generally designated 25 immersed in the liquid suspension. The coronode configuration is herein represented as three longitudinally situated knifeedge type electrodes *a*, *b*, and *c*, a substantial portion of which in each instance is overcoated with a dielectric material 27. Although various electrode spacings may be employed, the edge of the knife-like electrodes will generally be located from about 5 to about 50 mm. from the surface of the imaging electrode 1 with optimum results being achieved at spacings of about 10–20 mm. The imaging electrode 1 and container 12 containing the liquid developer are so situated such that the surface of the developer 13 at least contacts the surface of the imaging electrode in a plane which passes tangent to the surface of the imaging electrode. The spacings of the coronodes *a*, *b*, and *c* from one another may range from about 5 to 50 mm. depending upon the surface area contact which the imaging electrode makes with the liquid developer. Although the preferred polarity of operation is with the immersed coronode system negative and the imaging electrode positive, generally the same image sense occurs with the reverse polarity. Thus, the negative polarity of the immersed coronode is only a preferred embodiment.

The image 30 formed on the surface of the imaging electrode is carried so as to contact copy web 32 which is passed up against the surface of the imaging electrode by two idler rollers 33 and 34 in a manner such that the web moves at the same speed as the periphery of the imaging electrode drum. A transfer roller 35 is

placed behind the web and between the idler rollers. Thus, the developed image may be pressure transferred from the surface of the imaging electrode to that of the copy web. Although for purposes of the present illustration this is the means that is shown any suitable technique may be used to transfer the developed image. For example, the transfer step may be carried out by exposure of the developed image to an actinic radiation source of the necessary wavelength to transfer the photosensitive pigment particles from the imaging electrode to the copy web or the particles may be transferred by an adhesive pickoff technique.

Any suitable means may be used to fix the image formed on the copy web such as by placing a lamination over the top surface of the transferred image or by heat or vapor fusing the resulting pigment to the underlying substrate. The fixing step is represented in the present illustration by a fixing unit 36. The remnants of the image are removed from the surface of the imaging electrode by a brush 37. The surface of the imaging electrode is then ready to undergo another imaging cycle.

FIG. 2 represents a continuous imaging process of the present invention used in a polychromatic imaging mode. There is seen an endless transparent conductive belt or electrode configuration generally designated 50 which in this instance consists of a transparent conductive support 51, such as Mylar, overcoated with a thin layer of optically transparent aluminum 52. The belt 50, when in operation, is generally driven at a uniform velocity by any suitable means, such as by motor represented as 53, in the direction indicated by the arrow. The endless transparent belt is supported by rollers 54, 55, 56 and 57 with the motor being connected to one or more of the rollers. The support rollers contact only the edges of the endless belt thereby allowing the system to operate while avoiding contact with the working surface of the belt. Located within the inner area of the flexible belt apparatus are three exposure sections generally designated 57, 58 and 59 comprising a visible light source, shield, and corresponding lens system. Appropriate filters 61, 62 and 63 selectively direct the actinic radiation through slit exposure stations 64, 65 and 66 onto the transparency 67 to be printed, shown positioned on the inner surface of the transparent belt. Situated beneath the transparent belt directly opposite the appropriate exposure station are three developer troughs 68, 69 and 70 containing the liquid developer dispersions 71, 72 and 73. A high voltage source 80 connects the conductive layer 52 of the flexible belt with each of the coronodes 74, 75 and 76 immersed in the liquid developer troughs. By controlling the potential applied by voltage source 80 the surface of the liquid developer in each instance is selectively deformed in such a manner and to such a degree so as to contact the flexible belt at the position where the transparency 67 becomes exposed through the slit stations 64, 65, and 66, respectively, so as to externally control the amount of developer which is applied to the surface of the exposed flexible belt while applying various colored developers separately in proper sequence. As the transparency 67 passes beneath each exposure station the corresponding color pigments will be deposited upon the outer surface of the transparent electrode 50 with the final copy being a combination of the various pigments with the necessary built in registration. For example, utilizing a red filter at exposure station 57 and

a cyan pigment in the developer contained in trough 68, the cyan pigment will remain in the dispersion where red light is absorbed and will be deposited on the belt in the remaining non-illuminated areas. Employing a green filter and magenta pigment at the second station and a blue filter and yellow pigment at the third station similar results are obtained. In this manner the proper combination of pigments will be deposited on the belt-like electrode in registration to produce a color copy of the original transparency 67. The image developed on the surface of the flexible belt is then transferred by exposure to an actinic radiation source 77 to the copy web 78 driven by idler rollers 79 and 80, backed up by transfer roller 81. The surface of the imaging electrode is then cleaned by brush 82 and prepared for a new cycle.

Although the immersed coronode system of the present invention is represented in the illustrations as having knife-like surfaces from which the charges are emitted, any suitable configuration may be employed which achieves the necessary effect. Thus, a series of needle-like coronodes may be employed to provide the necessary image density or a thin-wire coronode may be used such as a corotron wire. In the latter instance it is generally desirable to utilize an insulated shield to partially enclose the corotron wire to direct the charge to the desired areas while preventing unnecessary loss of energy.

A wide range of voltages may be employed in the present system. For good image resolution, high image density and low background, it is preferred that the potential applied be such as to create an electric field of at least about 300 volts per mil across the imaging suspension. The applied potential necessary to attain this field strength will vary depending upon the spacing between the electrodes within the system as well as the shape and number of immersed electrodes. For the very highest image quality, the optimum field is at least about 2,000 volts per mil or higher. The upper limit of the field strength will be determined only by the breakdown potential of the suspension. Thus, where the immersed coronodes are spaced approximately 1 mil from the imaging electrode a potential of about 300 volts applied between the electrodes-coronode system will produce a field across the suspension of about 300 volts per mil.

In order to obtain the desired field strength and current density it is necessary that the coronode or coronodes immersed in the liquid imaging dispersion be such that there is a single direction whereby charges are emitted in one direction either from a point source or similar line source of energy. At least one of such coronodes must be included in the system. The sense of the image developed on the transparent electrode remains the same whether the point source electrode is positive or negative. The polarity of the field generally has no substantial effect upon this aspect of the process. Ordinarily, the only determining and effective limiting factor is the strength of the field applied. The polarization induced in the pigment particle switches with the field.

Any suitable material may be used as the transparent electrode in the system of the present invention. Typical optically transparent conductive materials include optically transparent glass overcoated with a thin conductive layer such as tin oxide, copper, copper iodide, gold or the like, cellulose acetate (optical grade), poly-

esters such as Mylar, a polyethylene terephthalate commercially available from E.I. duPont de Nemours & Co., and polycarbonates, such as Plestar, commercially available from General Aniline and Film Co. overcoated by any suitable means such as by vacuum deposition with a transparent metallic coating such as aluminum, copper, gold, silver or chromium. Other suitable materials including many semiconductive materials such as raw cellophane, which are ordinarily not thought of as conductors but which are still capable of accepting an injected charge carrier of the proper polarity under the influence of an applied field, may be used in the course of the invention. However, as mentioned above, the use of the more conductive materials is preferred because it allows for cleaner charge separation and the charge leaving the particles upon exposure can move into the underlying surface and away from the particles in which or from which they originated. This also prevents possible charge buildup on the electrode which might tend to diminish the entire electric field.

Any suitable substantially insulating carrier liquid may be used in the course of the present invention. Typical saturated hydrocarbons found suitable include: decane, dodecane, N-tetradecane, molten paraffin, molten beeswax or other molten thermoplastic materials, Sohio Odorless Solvent (a kerosene fraction commercially available from Standard Oil Co. of Ohio), Isopar G (a long chain saturated aliphatic hydrocarbon available from Humble Oil Co. of New Jersey) and mixtures thereof. Other substantially insulating carrier liquids which may be used comprise generally non-volatile, unsaturated, natural occurring oil-like organic compositions having a hydrocarbon nucleus. Typical materials include olive oil, castor oil, linseed oil, peanut oil, corn oil, and soybean oil. These compositions generally fall into the class of compounds known as glyceride esters of unsaturated fatty acids in which one or more of the hydroxyl groups of the glycerol constituent have been replaced by an acid radical. Other naturally occurring compounds which have been found useful include cotton seed oil and china wood oil derived from the seeds of plants; pine oil and cedarwood oil which are generally terpene compounds; and marine oils such as sperm oil and cod liver oil.

Any suitable electrically 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, 2,10-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. Pat. No. 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'-methyl-phenyl) 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-diamino-triazine, 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-phenylethyl-amino) 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)-thiazolepanthraquinone, 4-(2'-hydroxyphenylmethoxyamino) anthraquinone; azo compounds such as: 2,4,6-tris (N-ethyl-N-hydroxyethyl-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-naphthylamide, 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-naphthylamide; 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'-carbethoxyphenylxanthenonium 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'-di[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''-naphthylamide); pyrenes such as: 1,3,6,8-tetracyanopyrene, 1,3-dicyano-6,8-dibromo-pyrene, 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 salts of 6-cyano-1(1'-sulfo-2-naphthylazo)-2-naphthol, calcium lake of 1-(2'-azonaphthalene-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 sulfo-selenide, 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-oxiadazole; N-isopropylcarbazole; polyvinylanthracene; triphenylpyrrol; 4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinone; 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-mercaptobenzthiazole; 2-phenyl-4-alpha-naphthylidene-oxazolone; 2-phenyl-4-diphenyl-idene-oxazolone; 2-phenyl-4-p-methoxybenzylideneoxazolone; 6-hydroxy-2-phenyl(p-dimethyl-amino phenyl)-benzofurane; 6-hydroxy-2,3-di(p-methoxyphenyl)-benzofurane; 2,3,5,6-tetra-(p-methoxy-phenyl)-furo-(3,2f)-benzofurane; 4-dimethylaminobenzylidene-benzhydrazide; 4-dimethylaminobenzylideneisonicotinic acid hydrozide; furfurylidene-(2)-4'-dimethylamino-benzhydrazide; 5-benzylidene-amino-acenaphthene-3-benzylidene-amino-carbazole; (4-N,N-dimethylamino-benzylidene)-p-N,N-dimethylaminoaniline; (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)-tetrahydroimidazole; 1,3-diphenyl-2-4'-dimethyl amino-phenyl)-tetra-hydroimidazole; 1,3-di-(p-tolyl)-2-[quinolyl-(2'-)]-tetrahydroimidazole; 3-(4'-dimethylamino-phenyl)-5-(4''-methoxy-phenyl)-6-phenyl-1,2,4-triazine; 3-pyridyl-(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')]-1,3,3-triazole; 2,5-bis[4'-(N-ethyl-N-acetylamino)-phenyl-(1')]-1,3,4-triazole; 1,5-diphenyl-3-methylpyrazoline; 1,3,4,5-tetraphenylpyrazoline; 1-phenyl-3-(p-methoxy styryl)-5-(p-methoxy-phenyl)-pyrazoline; 1-methyl-2-(3',4'-dihydroxy-methylene-phenyl)-benzimidazole; 2-(4'-dimethylamine phenyl)-benzoxazole; 2-(4'-methoxyphenyl)-benzthiazole; 2,5-bis [p-amino-phenyl-(1)]-1,3,4-oxiadazole; 4,5-diphenyl-imidazolone; 3-amino-carbazole; copolymers and mixtures thereof.

Other photosensitive 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-dichloro-benzoquinone; anthraquinone-2-carboxylic acid, 4-nitro-phenol; maleic anhydride; metal halides of the metals and metal-

loids 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 thereon. 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 desensitized to narrow, broaden or heighten their spectral response curves.

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 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 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 desired to include other ingredients, such as spectral or electrical sensitizers or secondary colorants and secondary electrically photosensitive materials.

Any suitable proportion of electrically photosensitive particles to carrier liquid may be used. It is preferred that from about 2 to about 10 weight per cent particles be used for good balance between high image density and low background, consistent with particle economy. Optimum image quality has been obtained with from about 5 to 6 weight per cent particles.

The copy web material may consist of any suitable substrate upon which the final print is desired. Typical materials include Mylar (polyethylene terephthalate), Tedlar (polyvinyl fluoride), polyurethane, polyethylene, and ordinary bond paper.

To further define the specifics of the present invention the following examples are intended to illustrate and not limit the particulars of the present system. Parts and percentages are by weight unless otherwise indicated.

In the following examples, the imaging electrode consists of aluminized Mylar, as described above, unless otherwise stated. The immersed electrode will consist

either of a conductive steel knife-edge or a needle-like electrode, the base portion of which has been pre-coated with a dielectric material. A potential difference of about 7,000 volts is applied across the imaging suspension between the immersed electrode and the imaging electrode.

EXAMPLE I

A commercial, metal-free phthalocyanine is purified by acetone extraction to remove organic impurities. Since this extraction step yields a less sensitive beta crystalline form, the desired alpha form is obtained by dissolving 100 grams of the beta form in 600 cc.'s of sulfuric acid, precipitating it by pouring the solution into 3,000 cc.'s of ice water and washing with water to neutrality. The thus purified alpha phthalocyanine is then salt milled for 6 days and desalted by slurrying in distilled water, vacuum filtering, water washing, and finally, methanol washing until the initial filtrate is clear, thus, producing x-form phthalocyanine. After vacuum drying to remove residual methanol, the x-form phthalocyanine produced is used to prepare an imaging suspension according to the following formulation:

Phthalocyanine (x-form)	10	grams
Beta Carotene	0.3	grams
Sperm Oil (ADM 38 BW)	250	cc.
Tricresyl Phosphate	18	grams

The phthalocyanine is ground in a mortar, placed in a Waring Blender, with the other ingredients, and dispersed for about 10 minutes at high speed. The resulting suspension is poured into a shallow container in which there is immersed two needle like steel electrodes. A sheet of aluminized Mylar is placed so that the conductive surface of the substrate contacts the surface of the imaging suspension. The immersed needle electrodes are situated so that the point of electrodes are about 20 mm. from the imaging surface of the aluminized Mylar sheet. The potential as stated above is established and the suspension selectively exposed to a light intensity of about 10 foot-candles through a positive transparency with a General Electric visible light source. The aluminized Mylar electrode is maintained as the positive pole and the needle point electrodes the negative pole. By single material transfer a high quality negative image is formed on the surface of the aluminized Mylar.

EXAMPLE II

The process of Example I is repeated with the exception that the polarities of the electrodes in the system are reversed. There results, as in Example I, a negative image on the surface of the aluminized Mylar of a somewhat reduced quality.

EXAMPLE III

An imaging suspension of the following formulation is prepared:

Phthalocyanine (x-form)	4	grams
Olive Oil	20	cc.
Sperm Oil	56	cc.
Tricresyl Phosphate	4	grams
Beta Carotene	0.1	gram

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The resulting suspension is placed in a Waring Blender and dispersed for about 10 minutes at high speed. The dispersion is poured into a shallow container and the remaining portion of the configuration, set up as in Example I. The resulting imaging suspension is imaged through a negative transparency with the polarities similar to those established in Example I. There is produced a high quality positive image on the aluminized Mylar sheet.

EXAMPLE IV

The process of Example III is repeated with the exception that the aluminized Mylar is replaced with a NESA glass electrode. The resulting high quality positive image produced is similar to that obtained in Example III.

EXAMPLE V

The process of Example I is repeated with the exception that the following formulation is utilized.

Watchung Red B	1	gram
Phthalocyanine (x-form)	4	grams
Sperm Oil	80	cc.
Tricresyl Phosphate	20	grams
Beta Carotene	.05	grams

The needle-like electrodes of Example I are replaced with two knife-edge electrodes. Utilizing a negative transparency with the polarities the same as Example I, a high quality positive image is produced on the aluminized Mylar sheet.

EXAMPLE VI

The process of Example V is repeated with the exception that the following formulation is utilized.

Watchung Red B	1	gram
Algol Yellow	1	gram
Phthalocyanine (x-form)	4	grams
Tricresyl Phosphate	2	grams
Linseed Oil	106	cc.
Sperm Oil	80	cc.
Beta Carotene	.05	grams

With a negative color transparency at the input end, a high quality positive color image is produced on the aluminized Mylar sheet.

EXAMPLE VII

The process of Example VI is repeated with the exception that a NESA glass electrode is substituted for the aluminized Mylar sheet. The imaging quality of the process is again demonstrated.

EXAMPLE VIII

The x-form of phthalocyanine is prepared according to the process of Example I. Three separate imaging suspensions are prepared as follows:

Suspension No. 1		
Phthalocyanine (x-form)	4	grams
Sperm Oil	56	cc.
Olive Oil	20	cc.
Tricresyl Phosphate	4	grams

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-Continued

Suspension No. 1		
Beta Carotene	0.1	grams
Suspension No. 2		
Watchung Red B	1	gram
Sperm Oil	80	cc.
Tricresyl Phosphate	20	grams
Beta Carotene	.05	grams
Suspension No. 3		
Algol Yellow	1	gram
Tricresyl Phosphate	2	grams
Linseed Oil	106	cc.
Styrene	20	grams
Beta Carotene	.05	grams

Each suspension is poured into a separate trough, each trough containing a knife-edge type, longitudinally shaped electrodes. The three troughs are lined up parallel to each other, the first containing the phthalocyanine pigment, the second containing the Watchung Red pigment and the third containing the Algol Yellow pigment. Opposite each trough system is a corresponding filter, in the case of the phthalocyanine dispersion a red filter, the Watchung Red dispersion a green filter and the Algol Yellow dispersion a blue filter. Behind each filter is a visible light source. A thin transparent aluminized Mylar sheet is then passed between the filter systems and the trough system while simultaneously exposing a negative transparency which is fixed to the back of the aluminized Mylar substrate and thus passes synchronously with the latter. During the entire exposure process a voltage is applied to the electrodes immersed in the various pigment baths each electrode having a variable resistor included in the circuit so as to regulate the potential applied individually to each electrode. With the positive pole connected to the aluminized portion of the Mylar sheet and a negative pole to each of the immersed electrodes in the immersion baths the potential is so regulated that the imaging dispersion selectively kisses the surface of the aluminized Mylar substrate at the point of exposure to the transparency through the specific filter. A potential of about 7K volts is applied to the phthalocyanine dispersion, 7K volts to the Watchung Red dispersion and about 7K volts to the Algol Yellow dispersion. There is produced a high quality color print on the surface of the Mylar sheet.

Although the present examples were specific in terms of conditions and materials used, any of the above listed typical materials may be substituted when suitable in the above examples with similar results. In addition to the steps used to carry out the process of the present invention, other steps or modifications may be used, if desirable. For example, an insulating image can first be applied to the surface of the imaging electrode thus eliminating the necessity for exposure to a particular input, with image development realized in the conductive areas of the imaging electrode. In addition, other materials may be incorporated in the imaging suspension, the imaging electrode or the copy web to enhance, synergize, or otherwise desirably affect the properties of this system for their present use. For example, the imaging suspension may contain sensitizers for the photoconductive particles which are dissolved or suspended in the carrier liquid.

Anyone skilled in the art will have other modifications occur to him based on the teaching of the present

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invention. These modifications are intended to be encompassed within the scope of this invention.

What is claimed is:

1. A photoelectrophoretic imaging apparatus comprising in combination; an optically transparent electrode, means for presenting a photoelectrophoretic imaging suspension to said transparent electrode, said means comprising at least one container and spaced apart from said electrode, means to selectively deform the surface of a photoelectrophoretic imaging suspension so as to cause it to contact the imaging surface of

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said electrode, said means comprising at least one coronode positioned in said container, said coronode being spaced apart from and in electrical contact with said electrode, and means for projecting an image onto said electrode at the station where said electrode is selectively contacted by said imaging suspension opposite said coronode.

2. The apparatus as defined in claim 1 and further including means for transferring a developed image from the surface of said transparent electrode.

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