

[54] **INKING SYSTEM FOR LIQUID PARTICLE
MIGRATION ON AUTOMATIC MACHINES**

3,582,205 6/1971 Carreira..... 96/1 R
3,586,615 6/1971 Carreira..... 96/1 R

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[52] U.S. Cl..... **96/1 R, 96/1.3, 96/1.4,
117/37 LE, 355/3**

[51] Int. Cl. **G03g 13/14, G03g 13/22**

[58] Field of Search..... **96/1, 1.3, 1.4;
117/37 LE; 204/181**

[56] **References Cited**

UNITED STATES PATENTS

3,565,614 2/1971 Carreira et al..... 96/1.4

[57] **ABSTRACT**

An improved photoelectrophoretic imaging process is provided comprising adding sufficient additional insulating carrier liquid to the imaging suspension to maintain the concentration of said suspension substantially constant during the period of contact with an absorbent copy web.

8 Claims, 2 Drawing Figures

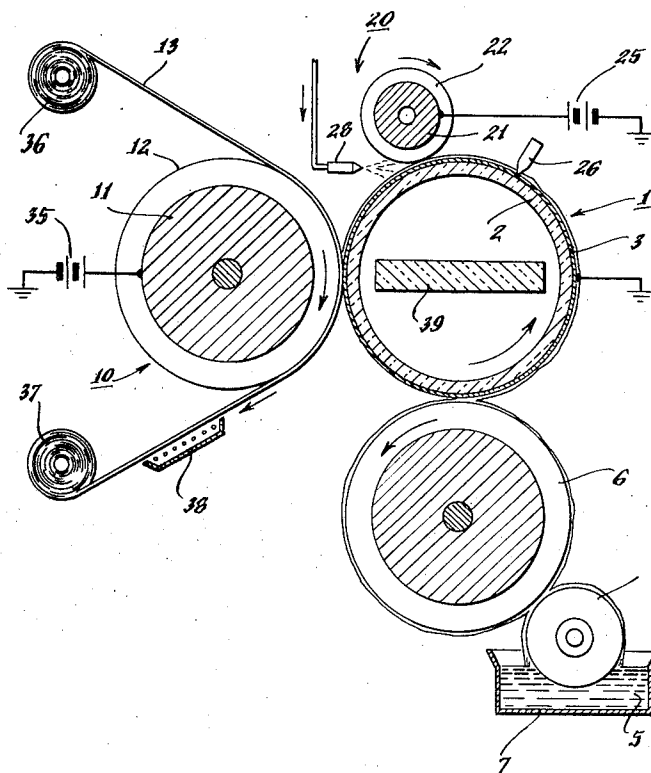


Fig. 1

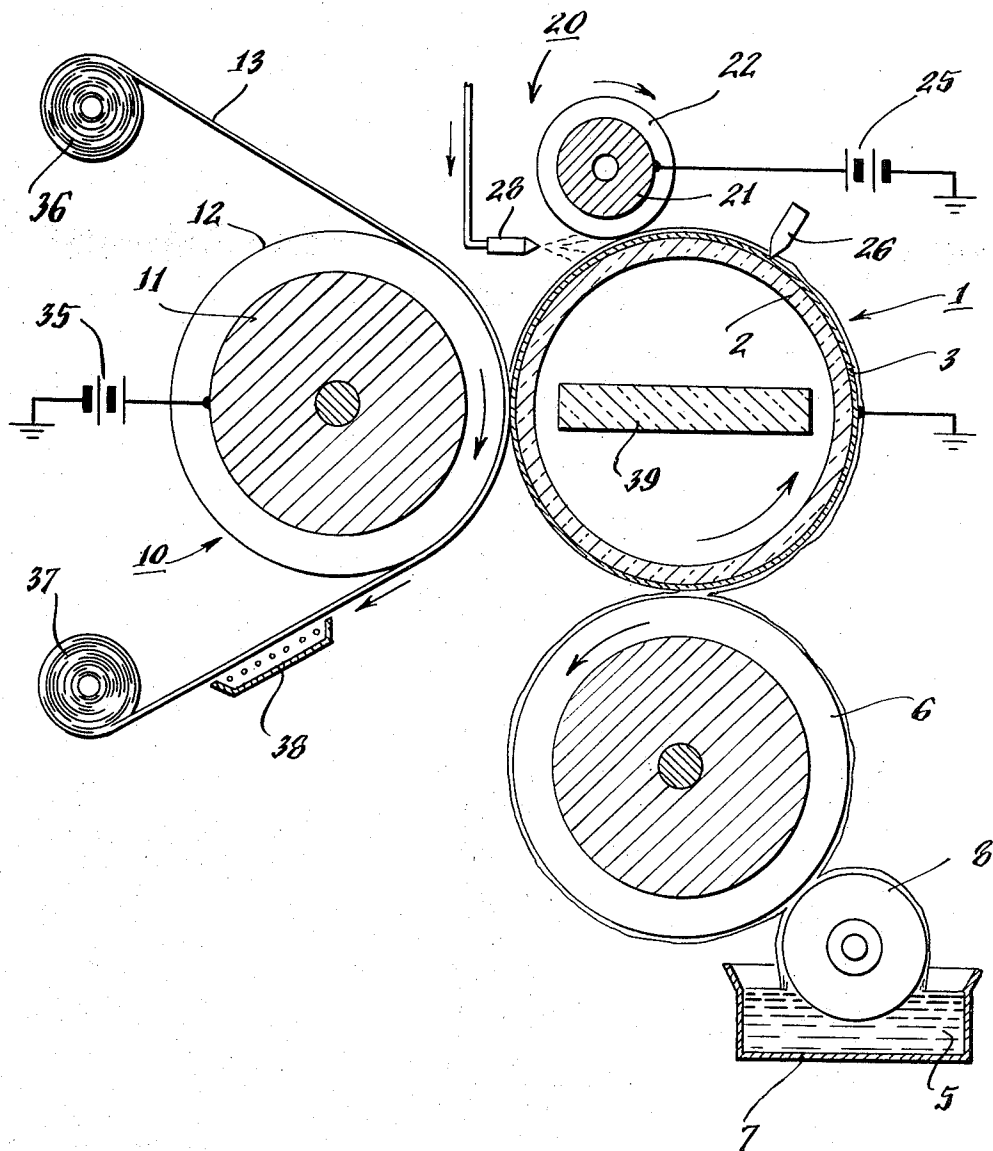
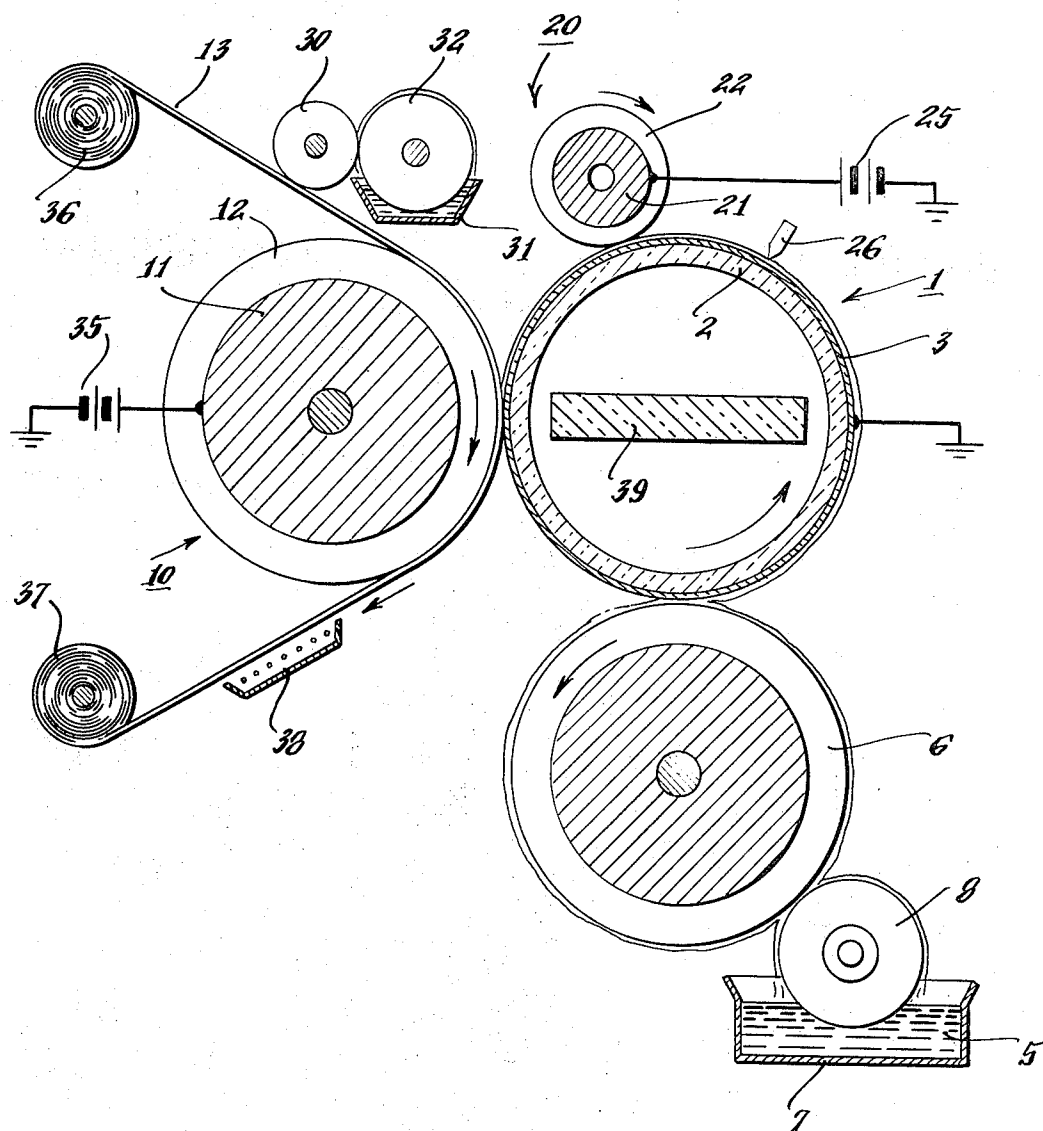


Fig. 2.



INKING SYSTEM FOR LIQUID PARTICLE MIGRATION ON AUTOMATIC MACHINES

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

In photoelectrophoretic imaging, colored photosensitive particles are suspended in an insulating carrier liquid. The suspension is then placed between at least two electrodes subjected to a potential difference and exposed to a light image. Ordinarily in carrying out the process, the imaging suspension is placed on a transparent electrically conductive support in the form of a thin film and an exposure is made through the transparent support while a second, generally cylindrically shaped biased electrode is rolled across this suspension. The particles are believed to bear an initial charge once 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 the base electrode so that the exposed particles migrate to the second or imaging electrode thereby forming images on each of the electrodes by particle subtraction, each image being complimentary, one 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 all of which will respond to the light to which the suspension is exposed. In the polychromatic imaging process, the imaging suspension contains a plurality of at least two differently colored finely-divided particles in the carrier liquid. Each of said particles comprising an electrically photosensitive pigment whose principal light absorption band substantially coincides with its principal photosensitive response. Thus, the pigment represents both the primary electrically photosensitive ingredient and the primary colorant for the specific particle in suspension. When the suspension is exposed to a multi-colored image, different colored particles absorb light of their complimentary color in the appropriate image areas and migrate to one electrode in proportion to the intensity of the light which they absorb, thereby leaving a full colored image behind corresponding to the original. An extensive and detailed description of the photoelectrophoretic imaging techniques as generally referred to may be found in U. S. Pat. Nos. 3,383,393; 3,384,488; 3,384,565; and 3,384,566, which are hereby incorporated by reference.

In the polychromatic system, a positive-to-positive imaging mode is generally employed wherein the useful image is that retained on the base or injecting electrode. A negative imaging mode, i.e., negative-to-positive imaging, is generally not suitable since the image taken from the imaging electrode results in reproductions which are not true color reproductions.

In monochromatic imaging, however, the positive-to-positive imaging mode is generally not preferred since the residual image on the injecting electrode tends to exhibit too much background. In the negative-to-positive imaging mode, however, excellent images are formed on the blocking electrode or upon a paper web interposed between the imaging suspension and the blocking electrode. In this mode, background can be controlled by pre-charging at both the bias or smoothing roller as described in co-pending application Ser.

No. 863,608 filed Oct. 3, 1969, now abandoned and at the imaging roller. The imaging roller charging is accomplished by corona "air breakdown" at the imaging nip. If for any reason this corona is suppressed, high background results. In contrast, however, in polychromatic photoelectrophoretic imaging, it is desired to suppress the corona developed at the imaging roller nip in order to prevent pre-charging of the pigments by atmospheric ions immediately prior to imaging which decreases the photoelectrophoretic image density. Since the desired image in polychromatic photoelectrophoresis is the image remaining on the transparent electrically conductive electrode, i.e., the injecting electrode, background from excess pigment on the imaging roller is usually no great disadvantage since this latter image is discarded. In U. S. Pat. No. 3,485,738, assigned to the same assignee herein, there is described an electrophoretic process wherein the air gap between the electrodes in an electrophoretic imaging system is filled with an insulating liquid before the electrodes are brought into proximity in the image forming area thereby preventing air ionization at the imaging nip. As described hereinabove, although the prevention of air ionization at the imaging nip is desirable in imaging on the injecting electrode as is customary in the polychromatic photoelectrophoretic imaging system, air ionization is necessary in imaging on the blocking electrode as in a negative-to-positive monochromatic photoelectrophoretic imaging system as a means of background control.

In photoelectrophoretic imaging, the ink particle density and the resulting image density are controlled by the original ink composition and the film thickness thereof on the transparent electrically conductive electrode. The rheology of the imaging suspension and its control prior to migration of particles, particularly with moving electrodes as in a continuous monochromatic photoelectrophoretic duplicator, has heretofore been a significant problem. The migrating particles must have sufficient mobility to reach the paper covered imaging roller, otherwise detachment from the transparent electrically conductive electrode is not accomplished and low density results. An undesirable situation arises when the concentration of particles in the imaging suspension gets so high that they impede each others free migration and thereby interfere with good imaging.

Accordingly, it is an object of the present invention to provide photoelectrophoretic imaging systems which overcome the above-noted deficiencies.

It is another object of the present invention to provide a photoelectrophoretic imaging system wherein the migration of the photosensitive particles within the liquid system is controlled.

It is still another object of the present invention to provide high quality images obtained by photoelectrophoretic imaging systems.

It is a still further object of the present invention to provide a photoelectrophoretic imaging system which provides enhanced image density without increasing background.

These as well as other objects are accomplished in accordance with the present invention where, in a method of photoelectrophoretic imaging comprising:

a. applying a layer of an imaging suspension to a first substantially transparent conducting electrode; said imaging suspension comprising finely divided electrically photosensitive particles in an insulating carrier liquid;

b. contacting the free surface of said imaging suspension with a second charging electrode;

c. applying a d.c. potential of sufficient amplitude to create a corona discharge between said second electrode and said imaging suspension;

d. removing said second electrode from said imaging suspension;

e. contacting the free surface of said imaging suspension with an absorbent web in the nip formed between said first electrode and a third imaging electrode;

f. applying a d.c. potential between said first and said third electrodes; and substantially simultaneously exposing said imaging suspension to a pattern of electromagnetic radiation until an image is formed;

the improvement is provided which comprises adding sufficient additional insulating carrier liquid to the imaging suspension to maintain the concentration of said suspension substantially constant during the period of contact with said absorbent web.

It has been found in the present invention that loss of the insulating carrier liquid in the imaging suspension due to absorption by an absorbent web, such as a paper web, during the imaging process increases the pigment concentration to a point where the charge exchange by the pigments is not sufficient to overcome the adhesion of the particles to the transparent electrically conductive electrode. Thus, in accordance with the present invention it has been found that the addition of additional insulating carrier liquid to the imaging suspension either at the bias or smoothing roller as hereinafter described or by moistening the absorbent web therewith prior to imaging, increases image density without increasing background.

The invention is further illustrated in the accompanying drawings wherein:

FIG. 1 illustrates a continuous monochromatic photoelectrophoretic duplicator operating in accordance with one embodiment of the present invention;

FIG. 2 illustrates a continuous monochromatic photoelectrophoretic duplicator operating in accordance with an alternate embodiment of the present invention.

Referring now to FIG. 1, there is shown a continuous monochromatic photoelectrophoretic duplicator comprising a transparent injecting electrode 1, an imaging electrode 10 and a biased charging electrode 20. The transparent electrode 1, in the instant illustration, is represented as consisting of a layer of optically transparent glass 2 overcoated with a thin optically transparent electrically conductive layer of tin oxide 3. Tin oxide coated glass of this nature is commercially available from Pittsburgh Plate Glass Co. under the trade name "NESA" glass. A uniform layer of an imaging suspension 5 is coated on the surface of the transparent electrode 1 by an applicator roller 6 of any suitable design or material, such as a urethane coated cylinder, which may rotate in the opposite direction, as herein represented, or the same direction as the transparent cylinder. The function of the ink applicator 6 is to apply a thin film of the imaging suspension from ink sump 7 by way of roller 8 to the transparent cylinder. In close proximity to the transparent roller electrode 1 is a rotary imaging electrode 10 having a conductive central core 11 which is covered with a layer 12 of material capable of blocking or limiting d.c. current such as polyurethane, which will be referred to as a blocking layer. Although a blocking layer such as this need not be used in the system, the use of such a layer is pre-

ferred because of the markedly improved results which it is capable of producing. A detailed description of the improved results and the types of materials which may be employed as a blocking layer may be found in U. S. Pat. No. 3,383,993.

The imaging suspension consists of a dispersion of specifically colored, finely divided electrically photosensitive particles in an insulating carrier liquid or vehicle. Any suitably differently colored photosensitive pigment particles may be used such as disclosed in U. S. Pat. Nos. 3,384,566 and 3,384,565. When the system is to be used in the preferred mode, i.e., in conjunction with monochromatic negative-to-positive photoelectrophoretic imaging, then the imaging suspension will contain a plurality of pigment particles in a carrier liquid, the pigment portion of which provides both the photosensitivity and the colorant property for the particle. In the case of a polychromatic system, the suspension will contain a plurality of at least two differently colored particles having similar properties to those used in the monochromatic process. Inasmuch as high image density and background reduction are the primary effects realized in the present invention, the preferred mode of operation is with imaging occurring at the surface of the electrode which contacts only the clear vehicle, that being the surface of the imaging electrode, or upon an absorbent web interposed between said imaging electrode and the imaging suspension as represented in the drawing. In an alternate embodiment, the suspension may be coated on the imaging electrode as depicted in U. S. Pat. No. 3,427,242 with the appropriate biased electrodes added, whereby the color image is produced directly by migration of the image particles to the surface of the transparent roller electrode. Although not preferred, the latter alternate embodiment demonstrates the versatility of the system. If desired, a multicolor image may be prepared employing several monochromatic imaging techniques in registration.

The primary objecting of the present invention is to maintain the imaging suspension at a substantially constant concentration during the period of contact with the absorbent web. Generally, a concentration of the pigment in the imaging suspension of from about 2 to about 10 percent by weight of the imaging suspension has been found to produce satisfactory results.

An absorbent web 13 is driven between roller electrodes 1 and 10 as represented, with an ink image being selectively deposited on the receiver sheet in the imaging zone. A reverse image pattern consisting of residual pigment particles is left behind on the NESA glass cylinder and can be wiped off at the ink application station. Thus, the applicator performs both the ink application and residual image removal steps.

Located in close proximity to the area of contact between the transparent and imaging electrodes is a biased charging electrode designated 20 consisting of a conductive central core 21 covered with a layer of a dielectric material 22. Any suitable dielectric material may be used at this stage of the invention. Typical dielectric materials include elastomeric materials such as polyurethanes; silicone rubber; Neoprene, a type of elastomer based on polymers of 2-chlorobutadiene-1,3; fluorelastomers such as Dow Corning's fluoro-silicone elastomers and Viton available from DuPont; natural and vulcanized rubbers, vinyl fluoride polymers such as Tedlar (DuPont) and KYNAR (Pennsalt Corp.); poly-

esters; acrylonitrile polymers such as Hycar (B.F. Goodrich); as well as mixtures and copolymers thereof.

As the film of the imaging suspension 5 coated on the surface of the transparent electrode 1 passes beneath the charging electrode 20, a d.c. potential is applied to the latter electrode by potential source 25. The effect of the resulting field and established corona current across the air gap and the imaging suspension is to charge substantially all the photosensitive particles present in the imaging suspension to the polarity of the charging roller 20 and, in addition, to concentrate the particles at the surface of the transparent electrode 1 by electrophoretic migration. Thus, a layer of highly concentrated, largely unipolar pigment is deposited on the transparent electrode 1 with a layer of relatively clear liquid vehicle above it. When this layered suspension enters the imaging zone, i.e., the nip formed at the area of contact of the transparent electrode 1 with the imaging electrode 10, the layer contacting the potential image support surface, whether it be the electrode surface itself or an absorbent web interposed between the imaging electrode and imaging suspension as herein represented, will be substantially free of pigment particles thereby minimizing the possibility of contaminating the image support surface. A means 26 for metering the ink flow passing between the charging electrode 20 and the transparent electrode 1 can be included in the system to control total ink film thickness and to eliminate an excess of ink which otherwise tends to suppress corona thereby nullifying the effect of the corona current upon the imaging suspension.

As shown in FIG. 1, an array of spray nozzles 28 emits a spray of insulating liquid from a source (not shown) into the opening nip formed between the transparent injecting electrode 1 and the biased charging electrode 20. The spray is adapted to provide sufficient additional liquid vehicle to compensate for the potential vehicle absorption by the absorbent web. It has been found in the present invention that the absorption of ink vehicle by the absorbent web 13, results in a concentration of the imaging particles and interferes with the photoelectrophoretic control of their deposition. Although it is impossible to measure local viscosity of the ink in an imaging nip, it is currently believed that this viscosity is increased by such vehicle loss, and that the resultant loss of free particle mobility interferes with the imaging process. Whatever the detailed explanation, the deleterious effects of vehicle absorption may be counteracted, according to the present invention by adding additional vehicle-compatible fluid between the imaging suspension and the absorbent receiving sheet. The amount of fluid to be added must be limited, however, to a level where corona discharge in the nip may still occur. If sufficient liquid is added to suppress corona, the background tends to rise undesirably.

In an alternate embodiment of the present invention as shown in FIG. 2, the array of spray nozzles 28 is omitted and in lieu thereof, the additional insulating liquid is applied directly to the absorbent web 13 via a moistening roller 30. Moistening roller 30 is also adapted to supply a sufficient amount of insulating liquid to the web to compensate for the insulating liquid normally absorbed from the imaging suspension by the web in the imaging nip. The moistening roller 30 receives insulating liquid from insulating liquid sump 31 by way of roller 32. In this manner, insulating liquid is

applied to the web 13 in sufficient amounts to moisten the web with insulating liquid thereby overcoming the normal tendency of the web to absorb insulating liquid from the imaging suspension within the imaging zone. In this manner, migration of the pigment particles is allowed to occur under controlled conditions which permit optimum image density with low background density to be obtained. Although application of the additional insulating liquid has been shown by means of spraying or moistening rollers, any means for dispensing the insulating liquid can be employed such as brushing, dipping, use of porous ink dispensing cartridges, padding and other similar systems.

The amount of insulating liquid added by either the spray nozzles to the imaging suspension or via the moistening roll to the absorbent web is not considered narrowly critical. However, sufficient insulating liquid should be added to compensate for the vehicle absorption by the paper web within the imaging zone. Excessive addition of insulating liquid is to be avoided since this will result in a suppression of the corona generated air breakdown in the imaging nip which is required to control background. Generally, from about 0.001 to about 0.01 gram of insulating liquid per square inch of surface of the transparent electrode containing the imaging suspension or per square inch of the absorbent web which contacts the imaging suspension in the imaging nip has been found satisfactory. Greater or lesser amounts of insulating liquid can be added depending upon the absorptive nature of the web and the thickness thereof. For example, at printing speeds of about 10 to 15 inches per second a non-absorptive paper will typically pick up about 0.1 gram of liquid over the total surface area of an 8 1/2 inches by 11 inches sheet; whereas, a highly absorptive paper of the same size could pick up about 0.5 gram. Both the spray and the moisture roll can be adapted by various metering devices to provide the necessary quantity of insulating liquid.

The additional insulating liquid can be added at any point in the system which will ultimately contact the imaging suspension in the imaging zone. Thus, the additional insulating liquid can be added directly to the imaging suspension (FIG. 1) or to the absorbent web (FIG. 2). It is considered preferable to avoid adding the insulating liquid directly into the imaging nip, as this may cause suppression of corona and thus increased background.

The potential applied to the charging electrode 20 is generally maintained at a value above the corona threshold potential for the air gap between the film of imaging suspension and the charging electrode 20. The primary concern is that sufficient d.c. corona current be generated to cause the particles in this suspension to become unipolar and to establish a thin, clear layer of vehicle between the particle suspension and the absorbent web 13. For example, when a 3/16 inch thick layer of polyurethane is used to cover the charging roller 20 and a 4 mil thick absorbent paper web is used together with a 1-2 micron film of imaging suspension, voltages to be applied to the charging electrode generally range between about 2500 and 8500 volts, the preferred range being from about 5600 to about 7500 volts. The polarity of the potential applied to the charging electrode 20 is generally maintained at the same sense as that applied to the imaging electrode 10.

The layered suspension supplemented by insulating liquid in the manner shown in FIG. 1 enters the imaging zone between the transparent and imaging electrodes where an image is projected into the nip of the rollers by way of a first surface mirror designated 39. A field is established across the imaging zone as a result of power source 35. Through the entire operation, the NESAs glass roller electrode is connected to ground. The absorbent web 13 represented in the form of a paper web is fed from supply roll 36 and passes between the injecting electrode and the imaging electrode and is rewound on takeup roller 37. Fixing of the image developed on the surface of the paper web 13 may be accelerated by the presence of heating unit 38 which assists in vaporizing the insulating liquid remaining in combination with the colored pigment particles. Heating unit 38 also effectively removes all additional insulating liquid added via spray nozzles 28 or moistening roll 30.

Although the charging electrode 20 may be positioned generally at any point between where the imaging suspension is coated onto the transparent electrode and the imaging zone, it is preferred that roller 20 be located as close as possible to the area of contact between the imaging electrode and the transparent injecting electrode so as to decrease the time for dark discharge of the unipolar particles to occur prior to imaging.

Any suitable insulating carrier liquid can be employed in the course of the present invention. Typical vehicles include Sohio 3454 Odorless Solvent, a kerosene fraction available from Standard Oil Company of Ohio, Isopar G, a branched chain saturated aliphatic hydrocarbon mixture available from Humble Oil Co. of New Jersey, volatile silicone oils such as dimethylpolysiloxane (Dow Corning Co.) fluorinated hydrocarbons such as Freon (DuPont) and compatible mixtures thereof and the like.

A wide range of voltages can be applied between the electrodes in the system to effect imaging. In the case of the field established across the imaging suspension in the imaging zone, it is preferred, in order to obtain good image resolution and density that the field across the imaging suspension be at least about 5 volts/micron and preferably more than about 12 volts/micron. The applied potential necessary to obtain the strength of field will of course vary depending upon the intra-electrode gap and upon the thickness and type of blocking material used on the imaging electrode surface. The preferred voltage to be applied to the charging electrode 20 normally exceeds the corona threshold which is typically about 3500 volts. Voltages as high as 8,000 volts have been applied to the charging and imaging electrodes to produce images of high quality. The upper limit of the field strength appears to be limited by the breakdown field characteristics of the suspension and blocking material.

When the imaging suspension passes between the transparent electrode and the charging electrode 20, the particles are caused to assume unipolar charge and are driven so as to uniformly deposit within the liquid carrier on the surface of the transparent electrode thus presenting a two-layered film with the vehicle being the most superficial or outermost layer. The additional insulating liquid added at this point blends readily with the outermost layer of vehicle with little or no disturbance to the layer of particles on the transparent elec-

trode. The diluted imaging suspension is then carried into the imaging zone between the transparent electrode and the imaging electrode. Imaging as carried out in conjunction with the process of the present invention will generally be in a negative-to-positive image mode, so as to deposit particles on the absorbent web in illuminated areas. Thus, for purposes of the present invention in order to produce a positive image on the receiver sheet, a negative image is projected through the imaging suspension at the imaging zone. As discussed above, a potential is applied across the imaging suspension and as a result of the exposure, the exposed pigment particles initially suspended in the carrier liquid and as a result of the effect of the charging electrode 20, now uniformly plated on the surface of the transparent electrode, migrate upon exposure to the actinic radiation through the carrier to the surface of the imaging roller or, in the instant of the above-described illustration, to the surface of the intervening receiver paper sheet. The pigment image formed, whether it be on a removable sheet of blocking material wrapped around the conductive core of the imaging roller or, as in the instant illustration, on a continuous receiver copy web, may be fixed in place, for example by placing a lamination over its top surface as by spraying with a thermoplastic composition, or by removal of residual solvent aided by the application of heat, or, if desired, the image may be transferred to a secondary substrate to which it is, in turn, fixed. The system herein described produces a high contrast image with little or no background in a negative-to-positive imaging mode. The images formed on the injecting electrode 1 and/or on absorbent web 13 may be optionally offset to secondary receiving sheets. Suitable electrostatic, adhesive, and other transfer means are well known in the art.

It is to be understood that it is not intended that the structural arrangement of the apparatus represented by the illustration be restricted to the design as set out herein and all similar configurations which will satisfy the requirements of the present invention are contemplated. For example, although the imaging electrode is represented as a cylinder, it may also take the form of, for example, a flat plate electrode or a flexible metallized Mylar belt as may the injecting or NESAs electrode.

When used in the course of the present invention, the term "injecting electrode" should be understood to mean that it is an electrode which will preferably be capable of exchanging charge with photosensitive particles of the imaging suspension when the suspension is exposed to light so as to allow for a net change in the charge polarity of a particle. By the term "blocking electrode or layer" is meant one which is substantially incapable of injecting charge carriers into the photosensitive particles when particles come into contact with the surface of said electrode. The use of the blocking layer serves to substantially eliminate particle oscillation in the system.

It is preferred that the injecting electrode be composed of an optically transparent material, such as glass, overcoated with a conductive material such as tin oxide, copper iodide, gold or the like; however, other suitable materials including many semi-conductive materials such as cellophane film, which are ordinarily not thought of as being conductive but which are still capable of accepting injected charge carriers of the proper polarity from the imaging particles under the influence

of an applied electric field may be used within the course of the present invention. The use of more conductive materials allows for cleaner charge separation and prevents possible charge buildup on the electrode. The blocking layer of the imaging electrode, on the other hand, is selected so as to prevent or greatly retard the injection of charge carriers into the photosensitive pigment particles when the particles reach the surface of this electrode. The core of the imaging electrode generally will consist of a material which is fairly high in electrical conductivity. Typical conductive materials include conductive rubber, and metal foils of steel, aluminum, copper and brass have been found suitable. Preferably, the electrode will have a high electrical conductivity in order to establish the required field differential in this system; however, if a material having a low conductivity is used, a separate electrical connection may be made to the back of the blocking layer of the blocking or imaging electrode. For example, the blocking layer or sleeve may be a semi-conductive polyurethane material having a conductivity of from about 10^{-8} to 10^{-9} ohm-cm. If a non-conductive core is used, then a metal foil may be used as a backing for the blocking sleeve. Although a blocking layer need not necessarily be used in this system, the use of such a layer is preferred because of the markedly improved results which it is capable of producing. It is preferred that the blocking layer, when used, be either an insulator or 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 its surface thereby preventing particle oscillation in the system. The result is enhanced image density and resolution. Even if the blocking layer does allow for the passage of some charge carriers to the photosensitive particles, it still will be considered to fall within the class of the preferred materials if it does not allow for the passage of sufficient charge so as to re-charge the particles to the opposite polarity. Exemplary of the preferred blocking materials used are baryta paper, Tedlar (a polyvinyl fluoride), Mylar (polyethylene terephthalate) and polyurethane. Any other suitable material having a resistivity of about 10^7 ohm-cm. or greater may be employed. Typical materials in this resistivity range include cellulose acetate-coated papers, cellophane, polystyrene and polytetrafluoroethylene. Other materials that may be used in conjunction with the injecting and blocking electrodes and other photosensitive particles which may be used as the photomigratory pigments and the various conditions under which the process operates may be found in the above cited patents, U. S. Pat. Nos. 3,384,565; 3,384,566; 3,384,448; and 3,383,993.

It is to be understood that any suitable photosensitive pigment particle as identified in the above-cited patents may be employed within the course of the present invention with the selection depending largely upon the photosensitivity and the spectral sensitivity required. Typical photoresponsive materials includes substituted and unsubstituted organic pigments such as phthalocyanines, for example, Monarch Blue G, beta form of copper phthalocyanine available for Hercules, Inc., quinacridones as for example on Monastral Red B available from DuPont, Algol Yellow (1,2,5,6-di (C,C'-diphenyl)-diazoanthraquinone) (C.I. 67300), Irgazine Red, tri-sodium salt of 2-carboxyphenylazo (2-naphthol-3,6-, disulfonic acid) (C.I. 16105), 3-benzylidene

aminocarbazole, 3-aminocarbazole, Watchung Red B (1,4'-methyl-5-chloroazobenzene-2'-sulfonic acid) -2-hydroxy-3-naphthoic acid) (C.I. 15865), a yellow pigment identified as Yellow 96 comprising N-2''-pyridyl-8,13-dioxo dinaphtho-(2,1-b; 2',3'-d)-furan-6-carboximide and inorganic pigments such as cadmium sulfide, cadmium selenide, selenium, antimony sulfide, arsenic sulfide, zinc oxide and mixtures thereof. The imaging suspension may contain one or more different photosensitive particles each having various ranges of spectral response.

The following examples further define, describe and compare the improved imaging systems of the present invention. Parts and percentages are by weight unless otherwise indicated.

In the following examples, the NESA electrode consists of a six inch diameter Pyrex glass cylinder concentric to about 0.001 inch having a conductive tin oxide coating thereon. The imaging or blocking electrode consists of a four inch diameter conductive steel core with a quarter inch thick layer of polyurethane forming the blocking layer. The biased electrode consists of a half inch diameter aluminum core covered with a quarter inch layer of polyurethane having a resistivity of about 10^9 ohm-cms.

EXAMPLE 1

An imaging suspension is prepared as follows; 6.0 grams of X-phthalocyanine as described in U. S. Re issue 27,117, which is incorporated herein by reference, and 75 cc. of Sohio 3454 solvent are placed in a paint shaker partly filled with 1/8 inch steel shot and are milled therein for one hour. Similarly, 8.0 grams of Irgazine Red and 75 cc. of Sohio 3454 solvent are placed in a paint shaker and are milled for two hours. Also, 3.0 grams of Algol Yellow in 50 cc. of Sohio 3454 solvent are placed in a paint shaker and are milled therein for one hour. Thereafter, the resulting pigment dispersions are admixed together with 25 cc. of Sohio 3454 solvent and 25 grams polyethylene AC-8 (Allied Chemical) and the resulting mixture is heated to 135°C. Thereafter, the mixture is cooled to room temperature (22°C.) and 50 grams Piccotex 100 (Pennsylvania Ind. Chem. Co.) dissolved in 50 cc. of Sohio 3454 solvent is added. 0.01 gram of β -carotene (Eastman Kodak Co.) and 6.0 grams of tricresyl phosphate (Union Carbide) are stirred into the mixture. The resulting black imaging suspension is applied to the tin oxide coated glass cylinder from a urethane sponge. The film of imaging suspension is metered to a thickness of about 3 microns. As the film passes the nip between the biased roller and the NESA electrode, a potential of about +7,000 volts is applied across the electrodes. The NESA electrode is rotated at a speed of 5 inches per second. Sterling Litho Paper (West Virginia Pulp & Paper Co.) is fed from a supply roll into the nip between the NESA electrode and the imaging roller and onto a wind-up roll. A spray of Sohio 3454 solvent is applied at the nip formed between the biased roller and the NESA electrode as shown in FIG. 1. The spray is metered so as to supply about 0.001 grams of solvent per square inch of the NESA electrode. As the imaging suspension proceeds into the nip formed between the NESA electrode and the paper web backed by the imaging electrode, a high contrast negative image is projected into the imaging zone. A field of about +5,000 volts micron is developed across the 2 micron thick im-

aging suspension during exposure. A 500 watt quartz iodine light source is employed to illuminate the film negative. The light is passed through an $f/4.5$ optical system and projected into the nip by way of a first surface mirror. The illuminated photosensitive particles in the imaging suspension are selectively deposited on the paper receiver sheet in the imaging zone as the paper passes through said zone at a rate of 10 inches per second. Sharp, clear images are obtained with a character density of 1.0 and a background density of 0.03.

EXAMPLE 2

The above procedure is repeated without the use of a spray of insulating liquid. Background density is now observed to be 0.02 and image density is 0.74.

The contrast density is thus improved by the process of the present invention from 0.72 to 0.95 leading to a very perceptible and pleasing effect on image quality.

EXAMPLE 3

The apparatus employed in Example 1 is modified to eliminate the spray of insulating liquid and to replace said spray by a moistening roll adapted to contact the paper web prior to its entry into the nip formed by the injecting electrode and the imaging electrode as shown in FIG. 2. The moistening roller applies Sohio 3454 solvent to the paper web which, in this instance, is newsprint. The moistening roller is adapted to apply about 0.005 gram of solvent per square inch of newsprint. All other operating conditions are substantially identical to those in Example 1 except that the imaging speed is 30 inches per second and a blue imaging suspension is employed which is prepared as follows:

the following ingredients are milled with 1/8 inch steel shot in a paint shaker for two hours; 10 grams x-phthalocyanine, 0.1 grams β -carotene, 6.0 grams tricresyl phosphate and 200 cc. Sohio 3454 solvent. High quality low background blue images are obtained with a character density of 0.81 and a background density of 0.02.

EXAMPLE 4

The above procedure is repeated without the use of a moistening roller. Background is now observed to be 0.02 and image density 0.43.

The contrast density is thus essentially doubled by the process of the present invention from 0.41 to 0.79.

The above examples illustrate that although ink particle density and resulting image density can be controlled by the original ink composition and film thickness, the migrating particles must have sufficient mobility to reach the paper covered imaging electrode otherwise detachment from the injecting electrode is not accomplished and low density results. In accordance with the present invention, the addition of insulating liquid compensates for the liquid absorption by the paper web and in this manner, significantly enhanced contrast density is obtained.

Although specific materials and conditions were set forth in the above exemplary processes for forming reproductions in accordance with the present invention. Various other imaging suspensions, conditions, electrode materials and processes such as those listed above may be substituted in the examples with similar results.

Other modifications 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.

We claim:

1. In a method of photoelectrophoretic imaging comprising:

- a. applying a layer of an imaging suspension to a first substantially transparent conductive electrode; said imaging suspension comprising finely divided electrically photosensitive particles in an insulating carrier liquid;
- b. contacting the free surface of said imaging suspension with a second charging electrode;
- c. applying a d.c. potential of sufficient magnitude to create a corona discharge between said second electrode and said imaging suspension;
- d. removing said second electrode from said imaging suspension;
- e. contacting the free surface of said imaging suspension with an absorbent web in the nip formed between said first electrode and a third imaging electrode;
- f. applying a d.c. potential between said first and said third electrodes of sufficient magnitude to create a corona discharge between said third electrode and said imaging suspension and of a polarity of the same sign as between said second electrode and said imaging suspension; and substantially simultaneously exposing said imaging suspension to a pattern of electromagnetic radiation until an image is formed on said third electrode; the improvement which comprises adding sufficient additional insulating carrier liquid to the imaging suspension to maintain the concentration of said suspension substantially constant during the period of contact with said absorbent web, but insufficient to cause suppression of the corona discharge between said third electrode and said imaging suspension, said additional insulating carrier liquid being added in an amount between from about 0.001 gram to about 0.01 gram per square inch of imaging surface of either said absorbent web or said first electrode.

2. Method as defined in claim 1 wherein the third electrode is covered with a blocking layer.

3. Method as defined in claim 1 wherein said additional insulating carrier liquid is added to the imaging suspension by spraying said additional insulating carrier liquid into the nip formed between said first and second electrodes.

4. Method as defined in claim 1 wherein said additional insulating carrier liquid is added to the imaging suspension by applying said additional insulating carrier liquid to the absorbent web prior to passage of said web into the nip formed by said first and third electrodes.

5. Method as defined in claim 1 wherein the concentration of pigment in the imaging suspension ranges from about 2 to about 10 percent pigment by weight of the imaging suspension.

6. Method as defined in claim 1 wherein a potential above the corona threshold potential for the air gap between the imaging suspension and the second charging electrode is applied to said second electrode.

7. Method as defined in claim 1 wherein the potential applied to the charging electrode ranges from about 2,500 to about 8,500 volts.

8. Method as defined in claim 1 wherein a field is established across the imaging suspension within the imaging zone of at least 5 volts/micron.

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