# United States Patent [19]

**Goffe**

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[54] **IMAGING PROCESS USING VERTICAL PARTICLE MIGRATION**


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**Related U.S. Application Data**

[63] Continuation of Ser. No. 254,999, May 19, 1972, abandoned, which is a continuation of Ser. No. 54,264, July 13, 1970, abandoned.

[52] **U.S. Cl.** ..... **346/74 ES,** 346/74 R

[51] **Int. Cl.** ..... **H04n 5/76,** H04n 3/16

[58] **Field of Search** ..... 96/1, 1.4; 204/181; 117/1.7, 17.5, 218; 250/49.5, 2 C, 363; 346/74 ES, 74 EB; 178/6.6 A



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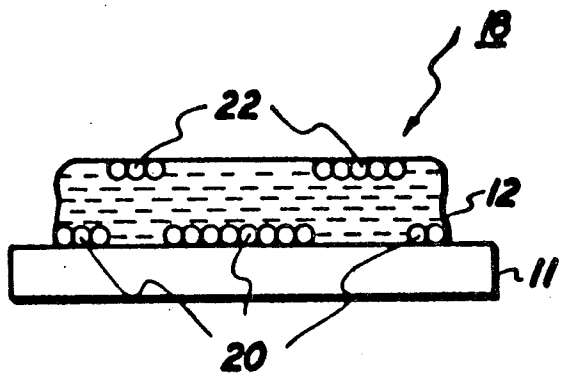
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[57] **ABSTRACT**

An imaging process wherein an imaging member comprising a liquid film supported on a substrate and in contact with migration material is employed. The migration material is caused to imagewise selectively migrate through the liquid film to the supporting substrate by subjecting the migration material to an imagewise migration force.


**12 Claims, 5 Drawing Figures**



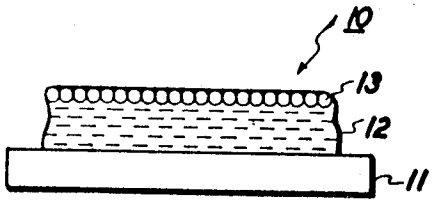



FIG. 1A

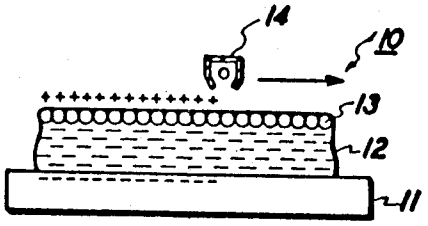



FIG. 1B

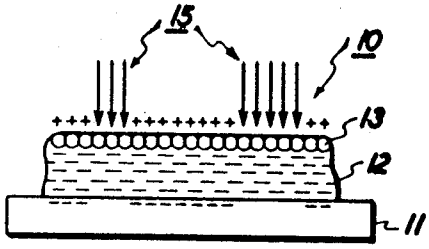



FIG. 1C

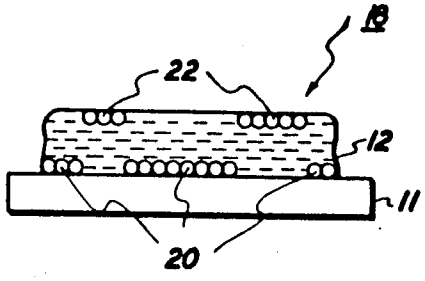



FIG. 2

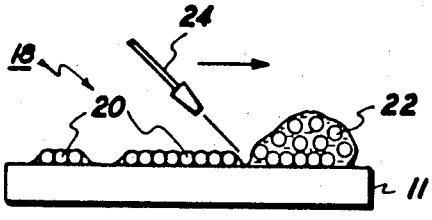



FIG. 3

# IMAGING PROCESS USING VERTICAL PARTICLE MIGRATION

## CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation of copending application S. N. 254,999 filed on May 19, 1972, now abandoned which is a continuation of application S. N. 54,264 filed on July 13, 1970, now abandoned.

## BACKGROUND OF THE INVENTION

This invention relates in general to the imaging and more particularly to a new migration imaging process. More specifically, this invention relates to migration imaging employing liquid migration layers.

There has recently been developed a migration imaging system capable of producing high quality images of high density, continuous tone and high resolution, embodiments of which are described in copending applications Ser. Nos. 837,591 and 837,780 both filed June 30, 1969. Generally, according to an embodiment thereof, an imaging member comprising a conducting substrate with a layer of softenable (herein also intended to include soluble) material, containing photosensitive particles overlaying the conductive substrate is imaged in the following manner: a latent image is formed on the photosensitive surface for example, by uniformly electrostatically charging and exposing it to a pattern of activating electromagnetic radiation. The imaging member is then developed by exposing it to a solvent which dissolves only the softenable layer. The photosensitive particles which have been exposed to radiation migrate through the softenable layer as it is softened and dissolved, leaving an image of migrated particles corresponding to the radiation pattern of an original, on the conductive substrate. The image may then be fixed to the substrate. For many preferred photosensitive particles the image produced by the above process is a negative of a positive original. These portions of the photosensitive material which do not migrate to the conductive substrate may be washed away by the solvent with the softenable layer. As disclosed therein, by other developing techniques, the softenable layer may at least partially remain behind on the supporting substrate.

There is disclosed in copending application Ser. No. 642,828 now U.S. Pat. No. 3,839,030 an imaging method utilizing an imaging member comprising a supporting substrate and an overlayer of electrically insulating softenable material containing photosensitive migration or fracturable material. According to the process disclosed therein, the imaging member is uniformly and electrostatically charged and then exposed to an imagewise pattern of activating electromagnetic radiation while the softenable material is soft whereby the photosensitive material migrates in depth in the softenable material in imagewise configuration to form a migration image. That is, while the material through which the photosensitive material migrates in imagewise configuration it is characterized as softenable, the material is in fact in a soft condition such that it offers very little resistance or no resistance to the migration force placed upon the photosensitive material. In other words the process described in copending application Ser. No. 642,828 eliminates the need for the softening step required in the migration imaging system referred to in copending applications Ser. Nos. 837,591 and 837,780.



An imaging system employing an imaging member having migration material in contact with a liquid film supported on a substrate is disclosed herein.

## SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide an imaging system utilizing an imaging member comprising migration material in contact with a liquid layer on a substrate to produce an image by means of imagewise migration of the migration material.

It is a further object of this invention to provide an imaging system wherein imagewise exposure of an imaging member and development of the image occurs simultaneously.

The foregoing objects and others are accomplished in accordance with this invention by providing an imaging member comprising migration material in contact with an electrically insulating liquid layer residing on a substrate. An imaging process is provided whereby an electrical image is placed upon the migration material whereupon the migration material migrates in accordance with said image to the substrate thereby forming an image. The unmigrated material can be removed by various means generally characterized as mechanical or electrical depending upon the migration material employed and the mechanical means convenient to the user.

In accordance with the imaging process disclosed in copending application Ser. No. 642,828 referred to above, an imaging member comprising a softenable layer having in contact therewith migration material can be caused to produce an image by placing a latent electrical image on the softenable layer while the softenable layer is soft, that is, in a physical state capable of permitting the migration material to migrate in response to a latent electrical image. According to the present invention, a latent electrical image is placed upon a liquid layer containing or in contact with migration material whereby the migration material migrates to a substrate supporting said liquid layer. Through the use of a liquid layer in the imaging members of this invention, the migration image can be formed by causing the migration material to imagewise migrate to the substrate by (a) subjecting the migration material to an imagewise migration force or by (b) subjecting the migration material to a migration force and imagewise changing the resistance of the liquid layer to the migration of migration material.

## BRIEF DESCRIPTION OF THE DRAWINGS

For a better understanding of the invention as well as other objects and further features thereof, references made to the following detailed disclosure of this invention taken in conjunction with the accompanying drawings wherein:

FIGS. 1A through 1C are partially schematic drawings representing a preferred method of forming a latent image on an embodiment of an imaging member, according to the optimum electrical-optical mode of migration imaging of this invention.

FIG. 2 is a partially schematic drawing representing an imaged member according to this invention.

FIG. 3 is a partially schematic drawing representing a method of removing the unmigrated migration material from the imaged member.

## DETAILED DESCRIPTION OF THE DRAWINGS

Referring now to FIG. 1*a*, there is shown a schematic drawing of one embodiment of an imaging member **10** according to this invention comprising substrate **11**, liquid layer **12** which contains at its upper surface particulate migration material **13**.

Substrate **11** may be electrically conductive or insulating. Conductive substrates generally facilitate the charging or sensitization of the member according to the optimum electrical-optical mode of the invention and typically may be of copper, brass, nickel, zinc, chromium, stainless steel, conductive plastics and rubbers, aluminum, steel, cadmium, silver, gold or paper rendered conductive by the inclusion of a suitable chemical therein or through conditioning in a humid atmosphere to ensure the presence therein of sufficient water content to render the material conductive. The liquid layer may be coated directly onto the conductive substrate, or alternatively, the softenable layer may be self-supporting and may be brought into contact with a suitable substrate during imaging.

The substrate may be in any suitable form such as a metallic strip, sheet, plate, coil, cylinder, drum, endless belt, moebius strip or the like. If desired, the conductive substrate may be coated on an insulator such as paper, glass or plastic. Examples of this type of substrate are a substantially transparent tin oxide coated glass available under the trademark NESA from the Pittsburgh Plate Glass Co., aluminized polyester film, the polyester film available under the trademark Mylar from DuPont, or Mylar coated with copper iodine.

The substrate may comprise any suitable electrically insulating material. Typical insulating materials include polyethylene, polypropylene, polyethylene terephthalate, cellulose acetate, paper, plastic coated paper, such as polyethylene coated paper, vinyl chloride - vinylidene chloride copolymers and mixtures thereof.

Liquid layer **12** can comprise a material which is at least in part liquid throughout the imaging process of the present invention. In some cases, upon appropriate radiation, the liquid can be caused to increase its viscosity to the extent that there is substantial increased resistance to migration when the migration force is placed upon the migration material. That is, the liquid layer of the imaging member of this invention need not be softened in order to reduce the resistance the layer offers to the migration material in opposition to the migration force which is placed upon the migration material by the process of this invention. When the migration force is non-electrical, for example, a magnetic force, the electrical resistivity of the liquid is not critical and can be either high or low in electrical resistivity. The liquid layer should have a high electrical resistivity so as to permit the migration material to retain any electrical charge it may receive in the process of this invention. Accordingly, it may be desirable to purify commercial grades of liquids so as to remove impurities which may impart a higher level of conductivity. This may be accomplished by running the fluids through a clay column or employing any other suitable purification technique. Generally speaking, the liquids employed in the liquid layer of this invention may consist of any suitable material having the aforementioned properties. The liquids may have either a high or low boiling point and includes such fluids as silicone oils ssuch as dimethyl-polysiloxanes and very high boiling point long chain aliphatic hydrocarbon oils ordinarily used as transformer oils such as Wemco-C transformer oil available from Westinghouse Electric Company. Any suitable volatile or non-volatile liquid may be employed. A preferred liquid is an aliphatic kerosene hydrocarbon fraction available from the Standard Oil Company under the tradename Sohio Odorless Solvent 3440. Other fluids include carbon tetrachloride, petroleum ether, Freon 214 (tetrafluorotetrachloropropane), other halogenated hydrocarbons such as methylenechloride, trichloroethylene, perchloroethylene, chlorobenzene, trichloromonofluoromethane, tetrachlorodifluoroethane. In addition, ethers such as diethyl ether, diisopropyl ether, dioxane, tetrahydrofuran, ethyleneglycol monoethyl ether, aromatic and aliphatic hydrocarbons such as benzene, toluene, xylene, hexane, chlorohexane, mineral oil, vegetable oil and mixtures thereof.

The above group of materials is not intended to be limiting, but merely illustrative of materials suitable for liquid layer **12**. The liquid layer may be of any suitable thickness with thicker layers generally requiring a greater electrostatic potential in the optimum and preferred modes of this invention. Thicknesses from about one-half to about 16 microns have been found to be preferred but a uniform thickness over the imaging area of about 1 to 4 microns has been found to provide for high quality images while permitting member construction. The liquid should not affect the migration material adversely such as exerting a solvent action or other reaction involving the integrity of the migration material or the substrate.

Liquid layer **12** may be formed by any suitable method including dip coating, roll coating, gravure coating and other techniques.

Migration material **13** may comprise any continuous or semi-continuous fracturable layer which is capable of breaking up into discrete particles of the size of an image element or less during the development of the image in accordance with this invention and permitting portions to migrate toward the substrate in image configuration. Preferably, migration material **13** is particulate but the mechanical characteristics of layer **13** may vary over a wide range. Although illustrated in a layered configuration in FIG. **1**, migration material **13** may also be in the form of a dispersion in a liquid in accordance with FIG. **4**. In the dispersed mode, dispersants known to those skilled in the art may be employed to maintain an adequate dispersion of the migration material and the liquid providing such dispersants do not interfere with the imaging method of this invention.

Migration material **13** comprises preferably particles in the range of from 0.01 to about 2.0 microns to yield images of optimum resolution and high density compared to migration images having particles larger than about 2.0 microns. For optimum resultant image density, the particles should not be above about 0.7 microns in average particle size. Layers of particulate migration material preferably should have a thickness ranging from about the thickness of the smallest element of migration material in the layer to about twice the thickness of the largest element in layer **13**.

Layer **13** may comprise any suitable material selected from an extremely broad group of materials and mixtures thereof including electrical insulators, electrical conductors, photosensitive materials and inert particles. For the modes hereof employing an electrical

migration force, the migrating portions of layer **13** should be sufficiently electrically insulating and/or non-charge injecting to hold their electrical migration force until the desired amount of migration has occurred. Conductive particles may be used if lateral conductivity is minimized by loose packing, for example, or by partly embedding only a thin layer of particles in layer **12** so that neighboring particles are in poor electrical contact.

Migration material preferably should be substantially insoluble in the liquid and otherwise not adversely reactive therewith.

Photosensitive materials for layer **13** permit the imaging members hereof to be latent imaged by the optimum electrical-optical mode hereof, to be further described, which is a simple, direct, optically sensitive method of producing high quality images according to this invention. Typical such photosensitive materials include inorganic or organic photoconductive insulating materials; materials which undergo conductivity changes when photoheated, for example, see Cassiers, Photog. Sci. Engr. 4. No. 4, 199 (1960) which is incorporated herein by reference; materials which photoinject, or inject when photoheated.

Photosensitive as used herein to describe materials for layer **13** more particularly means "electrically photosensitive." While photoconductive materials (and "photoconductive" is used in its broadest sense to mean materials which show increased electrical conductivity when illuminated with electromagnetic radiation and not necessarily those which have been found to be useful in xerography in a xerographic plate configuration) have been found to be a class of materials useful as "electrically photosensitive" overlayers in this invention and while the photoconductive effect is often sufficient in the present invention to provide an "electrically photosensitive" overlayer, it does not appear to be a necessary effect. Apparently the necessary effect according to the invention is the selective relocation of charge into, within and out of layer **13**, said relocation being effected by light action on the bulk or the surface of the "electrically photosensitive" material, by exposing said material to activating radiation; which may specifically include photoconductive effects, photoinjection, photoemmission, photochemical effects and others which cause said selective relocation of charge.

Any suitable electrically photosensitive material may be used herein. Typical such materials include organic or inorganic photoconductive insulating materials.

Preferred inorganic photoconductors for use herein because of the excellent quality of the resultant images include amorphous selenium, amorphous selenium alloyed with arsenic, tellurium, antimony or bismuth, etc.; amorphous selenium or its alloys doped with halogens; and mixtures of amorphous selenium and the crystalline forms of selenium including the monoclinic and hexagonal forms. Other typical inorganic photoconductors include cadmium sulfide, zinc oxide, cadmium sulfoselenide, cadmium yellows such as Lemon Cadmium Yellow X-2273 from Imperial Color and Chemical Dept. of Hercules Powder Co., and many others. Middleton et al. U.S. Pat. No. 3,121,006 lists typical inorganic photoconductive pigments. Typical organic photoconductors include azo dyes such as Watchung Red B, a barium salt of 1-(4'-methyl-5'-chloro-azobenzene-2'-sulfonic acid)-2-hydrohydroxy-3-napthoic acid, C.I. No. 15,865, a quinacridone, Monastral Red B, both available from DuPont; Indofast double scarlet toner, a Pyranthrone-type pigment available from Harmon Colors; Qunido-magenta RV-6803, a quinacridone-type pigment available from Harmon colors; Cyan Blue, GTNE, the beta form of copper phthalocyanine, C.I. No. 74,160, available from Collway Colors; Monolite Fast Blue GS, the alpha form of metal-free phthalocyanine, C.I. No. 74,100, available from Arnold Hoffman Co.; commercial indigo available from National Aniline Division of Allied Chemical Corp.; yellow pigments prepared as disclosed in copending application Ser. No. 421,281, filed Dec. 28, 1964, or as disclosed in Ser. No. 445,235 filed Apr. 2, 1965 both of which are incorporated herein by reference, X-form metalfree phthalocyanine prepared as disclosed in copending application Ser. No. 505,723, filed Oct. 29, 1965, quinacridonequinone from DuPont, sensitized polyvinyl carbazole, Diane Blue, 3,3'-methoxy-4,4'-diphenyl-bis (1'' azo-2'' hydroxy-3''-naphthanilide), C.I. No. 21,180, available from Harmon Colors; and Algol GC, 1, 2,5,6-di (D,D'-diphenyl)-thiazole-anthraquinone, C.I. No. 67,300, available from General Dyestuffs and mixtures thereof. The above list of organic and inorganic photoconductive photosensitive materials is illustrative of typical materials and should not be taken as a complete listing of photosensitive materials.

Any suitable photosensitive material or mixtures of such materials may be used in carrying out the invention, regardless of whether the particular material selected is organic, inorganic, is made up of one or more components in solid solution or dispersed one in the other, whether the layer is made up of different particles or made up of multiple layers of different materials.

Other materials which may be included in a photosensitive migration layer include organic donor-acceptor (Lewis acid-Lewis base) charge transfer complexes made up of donors 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-nitrophenol; 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.

As stated above, any suitable photosensitive material may be employed. In the optimum embodiment of a particulate, fracturable, migration layer, 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, multi-layers of particles in which the photosensitive material is included in one of the layers and where other layers provide light filtering ac-

tion 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 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. Other particle structures which may be used, if desired, include those described in U.S. Pat. No. 2,940,847 to Kaprelian. Also included are photosensitive materials wherein the change caused by radiation is permanent, persistent or temporary. Also included are those particles which are thermoconductive, that is, the material is changed by the heating effects of the incident radiation.

While photosensitive materials may be used in the preferred electrical migration force mode employing electrostatic images, any suitable non-photosensitive migration material such as graphite, dyes, starch, garnet, iron oxide, carbon black, iron, tungsten and mixtures thereof may also be used as described in copending application Ser. No. 483,675, filed Aug. 30, 1965 which is incorporated herein by reference and as further described herein.

It will also be appreciated that the migration of layer 13 may comprise a mixture of materials specifically chosen for their color to give a color imaging system. For example, see copending application Ser. No. 609,056, now abandoned filed Jan. 13, 1967 incorporated herein by reference.

Referring now to the imaging methods of this invention and how the materials of the migration layer of the imaging member described above is caused to migrate in depth in the liquid layer; broadly, the imaging methods of this invention can be divided into two modes; (A) applying to the migration material an imagewise migration force and (B) applying to the migration material a uniform migration force and imagewise changing the resistance of the liquid layer to migration of the migration material.

By either mode (A) or (B) above, there are a variety of forces which can be applied to and be made to act on the migration material to cause it to move in image configuration in depth through the liquid layer to the substrate of the imaging member. Such forces include electrical or electrostatic, magnetic, gravitational and centrifugal forces. An even greater variety of ways exist in which those forces can be made to act on the migration material either uniformly or imagewise. It has been found that the application of imagewise migration force or imagewise changing of the resistance of the liquid layer to a uniform migration force are the same as those employed when using imaging members containing a softenable layer in place of the liquid layer as described in the copending applications referred to above. Examples of methods of applying imagewise migration force to the migration materials are disclosed in copending application Ser. No. 837,780 referred to above which application is incorporated herein by reference. Briefly, such methods involve applying an imagewise charge to the migration material which produces an imagewise attraction of the migration material to the opposite polarity charges induced by the charges originally applied on the migration material; applying an imagewise external electric field acting on uniformly charged migration material; applying a uniform external electric field acting on imagewise charged migration material and applying an imagewise magnetic field acting on uniformly magnetized migration material.

It will be seen that the strength of an imagewise electrical or electrostatic migration force will depend upon the strength of the electric charge on or in the migration material and the strength of any external electrical field. The generation of the charge on or in the migration material may be affected by such factors as the distribution of the charge put on or in the structure including on or in the migration material; the ability of the migration material to hold a charge; the ability of the liquid layer to hold a charge and the magnitude of the electric field through the imaging member.

Modes of applying a migration force to the migration material hereof in mode (B) above where this force is accompanied by imagewise modification of the resistance of the liquid layer to the migration of migration material include such methods as applying a uniform charge to the migration which produces a uniform attraction of the material to induced charges of opposite polarity on the opposite of the liquid layer or on the substrate of the imaging member; applying an external electric field to act on the uniformly electrostatically charged migration material; applying magnetic fields acting on uniformly magnetized migration material; applying centrifugal forces on the migration material and applying gravitational forces on the migration material. In mode (B) it will also be seen that image-wise modification of the resistance to migration of the migration material through the liquid layer includes any change of the liquid layer or the migration material which directly or indirectly changes the liquid layer's viscosity during migration in the region in which the migration material moves or in which any other way changes the viscous drag of migration material in the liquid layer.

Although diagramatically illustrated in the attached drawings as FIGS. 1B and 1C, simultaneous charging and exposure of the imaging member of this invention is preferred when employing electrically photosensitive material as illustrated in the accompanying drawings. Referring more specifically to the imaging modes hereof and to FIGS. 1B and 1C, the latent image is formed by the electrical-optical mode hereof in an imaging member 10 with layer 13 comprising electrically photosensitive material by the method which comprises the steps of uniformly charging by means of a corona discharge device (FIG. 1B) with imagewise exposure simultaneously occurring (FIG. 1C). In FIG. 1B, the imaging member is uniformly electrostatically charged by means of corona discharge device 14 which is shown to be traversing the member from left to right, depositing a uniform positive charge on the surface of imaging member 10. Substrate 11, if conductive, is typically grounded as corona discharge device 14 traverses. For example, corona discharge devices of the general description and generally operating as disclosed in Vyverberg U.S. Pat. No. 2,836,725 and Walkup U.S. Pat. No. 2,777,957 have been found to be excellent sources of corona discharge useful in the charging of imaging member 10, both of which patents are incorporated herein by reference. Corona charging is preferred because of its ease and because of the consistency in quality in the images produced when corona charging is employed. However, any suitable source of corona may be used including radioactive sources as described in Dessauer, Mott, Bogdonoff Photo Eng. 6, 250 (1955)

which is incorporated herein by reference. However, other charging techniques such as induction charging, for example, as described in Walkup U.S. Pat. No. 2,934,649 are available in the art. The field within layer **12**, preferred for imaging, in the optimum mode hereof may run from a few i.e., about 5 volts/micron to as high as 200 volts/micron for both electrically conducting and insulating substrates. However, images of optimum quality result when the field within layer **12** is from about 40 volts/micron to about 100 volts/micron.

Where substrate **11** is an insulating material, charging of the member, for example, may be accomplished by placing the insulating substrate in contact with a conductive member, preferably grounded and charging as illustrated in FIG. **1B**. Alternatively, other methods known in the art of xerography for charging xerographic plates having insulating backings may be applied. For example, the member may be charged using double sided corona charging techniques where two oppositely charged corona charging devices one on each side of the member are traversed in register relative to member **10**.

Referring now to FIG. **1C**, as a second step in the embodiment of the optimum electrical-optical mode of forming the image, member **10** is exposed to an imagewise pattern of activating radiation **15** which is preferably simultaneous with the charging step in this embodiment.

Any suitable exposure level may be used. Exposures for optimum quality images will depend on many factors including the composition of photosensitive migration material **13**. Illustratively for amorphous selenium migration material, exposures between about 0.05 ergs/cm$^2$ to about **50** ergs/cm$^2$ of about 4,000 angstrom unit wavelength light and optimally between about 1 to about 10 ergs/cm$^2$ have been found to produce images of maximum density and contrast. Exposures exceeding about 1,000 f.c.s. may be preferred for photosensitive migration materials of composition other than the preferred materials comprising amorphous selenium. Lower exposures such as about one-half f.c.s. may be used for photosensitive migration materials comprising certain phthalocyanines.

Exposures may be from the migration material side or through the rear of a member, with a liquid layer and a support which are at least partially transparent to the activating radiation.

Uniform exposure or no exposure with uniform migration forces can be used with no image pattern present to result in films of desired optical density for desired colors. This provides an advantageous way of producing light filters or special light scattering structures.

Any suitable actinic electromagnetic radiation may be used. Typical types include radiation from ordinary incandescent lamps, X-rays, beams of charged particles, infra red, ultra violet and so forth.

A variation of the electrical-optical mode is to imagewise heat radiate in the exposure step a thermoconductive liquid layer and/or migration material, the electrical conductivity of which changes with temperature. Of course, imagewise heating may also be accomplished by non-exposure techniques such as contacting the structure to a heated member in an image configuration. The particles may become quickly discharged or changed in their ability to hold charge, or the discharge.

According to a preferred process embodiment of the preferred electrical migration force modes hereof, mode (A), an electrostatic image of a type similar to those found in xerography is placed in or on the imaging members hereof by any suitable means, typically which does not employ direct optical exposure of the imaging member, which does not destroy the functionality of the imaging members hereof including:

(i) charging in image configuration through the use of a mask or stencil;

(ii) first forming such a charge pattern on a separate photoconductive insulating layer according to conventional xerographic reproduction techniques and then transferring this charge pattern to the members hereof by bringing the two layers into very close proximity and utilizing breakdown techniques as described, for example, in Carlson U.S. Pat. No. 2,982,647 and Walkup U.S. Pat. Nos. 2,825,814 and 2,937,943;

(iii) charge patterns conforming to selected, shaped electrodes or combinations of electrodes may be formed by the "TESI" discharge technique as more fully described in Schwertz U.S. Pat. Nos. 3,023,731 and 2,919,967 or by techniques described in Walkup U.S. Pat. Nos. 3,001,848 and 3,001,849 and;

(iv) electron beam recording techniques, for example, as described in Glenn U.S. Pat. No. 3,113,179 or X-ray beam recording techniques wherein X-rays cause secondary emission of electrons which cause the subsequent deposition of charge on members hereof, for example, as described in Reiss, Image Production With Ionizing Radiation Through Electrostatic Accumulation from Electron Avalanches, Zeit. fur Angew. Phys. 19, 1, pp. 1–4 (1965), and Kaprelian U.S. Pat. No. 3,057,997.

The magnitude of the charge applied in this particular mode of forming an image need be only above the threshold to produce migration with the particular combination of materials used. As a practical matter, it is found generally to be preferred to apply a field within layer **12** of at least about 10 volts/micron to ensure optimum quality images while images have been produced with charge images producing a field within layer **12** below the 10 volt/micron figure and even below 4 volts/micron.

According to another mode hereof, oppositely charged image shaped electrodes may be disposed adjacent opposite sides of the imaging member to create an imagewise electrical migration force. Many specific modes of applying forces will occur to those skilled in the art upon a reading of this disclosure.

Proceeding now to the (B) mode hereof, imaging members hereof may be imaged by uniformly charging the member and selectively, in image pattern, physically altering, increasing or decreasing the permeability of the liquid layer to the migration of migration material before, during or after charging. Any suitable technique of imagewise changing the permeability of the liquid layer may be used including:

(i) imagewise hardening the softenable layer before or during charging, for example, by exposing certain liquid materials to an image pattern of ultra violet radiation to cause imagewise hardening, for example, by techniques described in Gundlach U.S. Pat. No. 3,307,941.

(ii) imagewise heating the liquid layer preferably after charging, for example, by exposing it to an infra red image pattern or by contacting it with a heated

member in image configuration. The migration material or liquid layer or the substrate or combinations thereof may absorb the infra red to cause the liquid layer to become heated thereby reducing its viscosity and resistance to migration of the migration material.

Depending upon specific materials employed in the imaging member and especially the material of layer **12**, other forms of actinic radiation may be used to selectively modify the permeability of layer **12** to particle migration. Suitable methods include: X-ray treatment, Beta ray treatment, Gamma ray treatment and high energy electron bombardment.

Referring now to FIG. **2**, there is diagrammatically illustrated an imaged member according to this invention. Shown in FIG. **2** is imaged member **18** containing migrated migration material **20** residing on substrate **11** while unmigrated material **22** remains in liquid layer **12.** In most instances it will be desirable to remove unmigrated material **22** together with unwanted liquid layer **12** after migration has occurred. Referring now to FIG. **3**, there is shown on substrate **11** migrated migration material **20** while unmigrated material **22** is being swept from the imaged member by means of an air knife **24.** Thus, it can be seen that one of the advantages in employing liquid layers in the migration imaging process is the ease of removal of the unmigrated material and unwanted liquid. Although diagramitically illustrated in FIG. **3**, a portion of liquid layer **12** remains on substrate **11.** Those skilled in the art can appreciate the various means of removing liquid from the substrate to the extent desired by means such as absorption into another body, evaporation or other means suitable to the environment to the particular imaging process. After removal of liquid layer **12** and unmigrated migration material **22,** the remaining migrated migration material **20** may be fixed to substrate **11** or transferred to another substrate and fixed thereon.

Alternatively, after migration has taken place, unmigrated material can be flushed from the imaging member with a clear liquid wash which can be the same or different than the liquid employed in the imaging member. In addition, after the migration image has been formed, the unmigrated migration material can be removed in imagewise configuration by contacting the migration imaged member to a receiver surface and transferring only the unmigrated particles. The unmigrated particles can be thus transferred by exerting an external force such as a magnetic field acting as in electrophoretic development can be employed. These external forces should be sufficiently weak so as not to overcome the coulombic and shortrange forces holding the migrated particles to the substrate of the imaged member.

As can be seen from the above, migration imaging members containing liquid films can be employed to produce migration images in a variety of ways. Preferably, the liquid employed has a viscosity below about $10^3$ poises although other liquids as described above can be employed.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples further specifically define the present migration imaging system. The parts and percentages are by weight unless otherwise indicated. All exposures are from a tungsten filament light source unless otherwise specified. The examples below are intended to illustrate the various preferred embodiments of the migration imaging method of this invention.

### EXAMPLE I

An imaging member is provided by first dispersing about 2 grams of air spun graphite particles, Type 200-19 available from the Joseph Dixon Crucible Company in about 10 ml. of a kerosene fraction available under the tradename of Sohio 3440 from the Standard Oil Company. The dispersed graphite in the kerosene is then spread on a 3 ml. alumunized Mylar film. The thus formed imaging member is placed beneath a movable corona discharge device and a stencil is inserted between the corona discharge device and the imaging member. The corona discharge device is activated and moved across the imaging member providing in the open image areas of the stencil a negative charge of about 200 volts on the imaging member while the aluminized layer on the polyester film is connected to the opposite pole of the corona discharge device. The migration particles in the charged areas of the imaging member migrate to the Mylar film upon being charged and remain there in imagewise configuration. The imaged member is then immersed in a reservoir of Sohio 3440 whereupon the unmigrated particles are washed from the film leaving behind the migration image adhering to the Mylar film.

### EXAMPLE II

The procedure of Example I is repeated except that the imaged member is passed beneath an air knife which blows the unmigrated migration material together with the kerosene fraction from the film leaving the migrated migration material adhering in image configuration to the Mylar film.

### EXAMPLE III

The procedure of Example I is repeated with the exception that the imaged member is subjected to a stream of clear kerosene fraction of the same type employed in the imaging member which flushes the unmigrated migration material from the imaging member leaving the migrated migration material adhering to the Mylar film.

### EXAMPLE IV

An imaging member is prepared by dispersing selenium particles having an average diameter of 0.5 microns in a hydrocarbon oil available from Westinghouse Electric Company under the tradename Wemco-C Transformer Oil. The dispersion is then spread on a 2 ml. thick film of polyethylene. The thus prepared imaging member is placed upon a conductive sheet and placed beneath a movable apertured corona discharge device. With the discharge device connected to the positive terminal of a voltage source and the conductive sheet connected to the negative terminal, the corona discharge device is passed over the imaging member while through the aperture of the corona discharge device an image is exposed to the imaging member by means of a slit scanning device. The unexposed areas of the imaging member receive a positive charge of about 100 volts and the particles in the unexposed areas migrate to the substrate in imagewise configuration. The unmigrated selenium particles together with the liquid are removed from the imaging member by

means of an air knife leaving behind in image configuration the migrated selenium particles on the film.

## EXAMPLE V

The imaging member of Example I is placed beneath a pin electrode corona discharge device with the aluminum coating on the Mylar connected to the opposite terminal of the power supply of the corona discharge device. The pin electrode is caused to move across the imaging member in image configuration placing in line configuration a positive potential of about 200 volts on the migration particles whereupon they migrate in image configuration to the substrate. The unmigrated migration material and liquid layer are removed by means of an air knife leaving the migrated migration material on the Mylar film.

## EXAMPLE VI

The procedure of Example IV with the exception that instead of dispersing the selenium particles in the transformer oil a semi-continuous layer of selenium is placed over the surface of the liquid film on the substrate by sprinkling the particles on the film. The particles of selenium remain on the surface of the film until a migration force is placed upon them causing them to migrate to the substrate in imagewise configuration. The unmigrated selenium and liquid film are removed in accordance with the procedure of Example IV.

Although specific components and proportions have been stated in the above description of preferred embodiments of the invention, other typical materials as listed above if suitable may be used with similar results. In addition, other materials may be added to the mixture to synergize, enhance or otherwise modify the properties of the imaging layer. For example, various dyes, spectral sensitizers or electrical sensitizers such as Lewis acids may be added to the several layers.

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. An imaging method comprising the steps of:

(a) providing an imaging member comprising a substantially electrically insulating liquid layer containing non-photosensitive migration material, on a substrate;

(b) then applying a uniform electrical imagewise migration force other than by a technique wherein an essential step is imagewise exposure to activating electromagnetic radiation, to said migration material whereby said migration material migrates without material lateral migration, in depth an imagewise configuration to said substrate leaving portions of said insulating liquid layer above areas of migration substantially devoid of migration material everywhere said uniform electrical imagewise migration force was applied.

2. The method according to claim 1 wherein said imaging member comprises non-photosensitive migration material dispersed in said liquid.

3. The method according to claim 1 wherein the migration force is applied to said migration material by means of a corona discharge device through a stencil.

4. The method according to claim 2 wherein said migration material is graphite.

5. The method according to claim 1 including the additional steps of removing the unmigrated migration material from said imaging member after imagewise migration occurs.

6. The method according to claim 5 wherein said liquid layer is removed together with the unmigrated migration material.

7. The method according to claim 5 wherein the unmigrated material is removed by contacting the imaged member to a receiver surface and inserting an external electric field acting on the unmigrated migration material.

8. The method according to claim 5 wherein said removal is accommplished by means of an air knife.

9. The method accoding to claim 5 wherein said removal is accomplished by immersing the imaged member in a liquid.

10. The method according to claim 5 wherein the average particle size of the migration material is between about 0.01 and 2.0 microns.

11. The method according to claim 10 wherein said liquid layer is in the range of from about one-half to about 16 microns in thickness.

12. The method according to claim 1 wherein said imagewise migration force comprises an imagewise electrical force supplied by means of a shaped electrode operatively associated with said imaging member.

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