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MIGRATION IMAGING SYSTEM WITH MOLTEN LIQUID DEVELOPMENT

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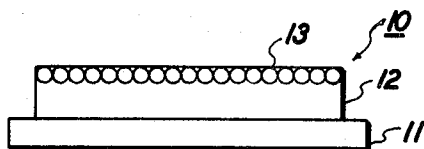


FIG. 1A

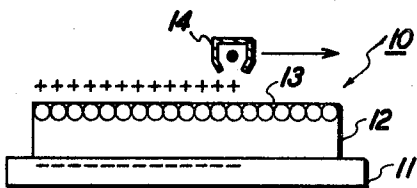


FIG. 1B

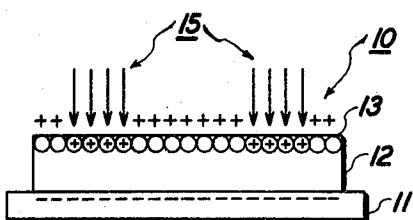


FIG. 1C

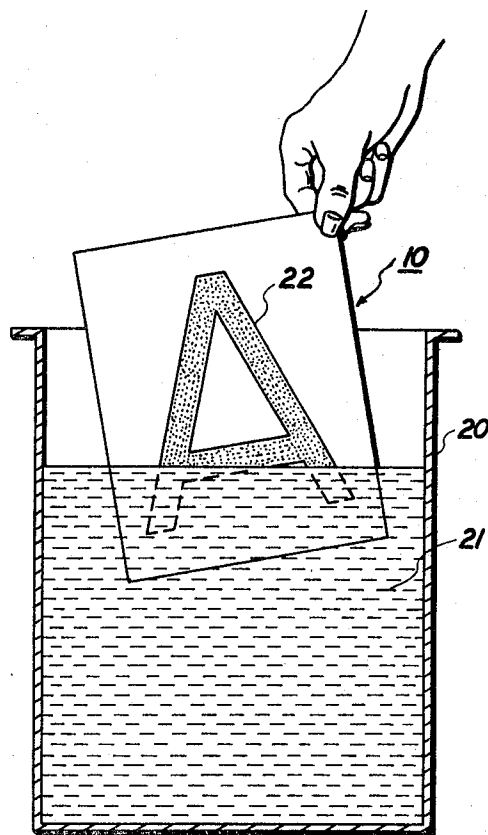


FIG. 2

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MIGRATION IMAGING SYSTEM WITH MOLTEN LIQUID DEVELOPMENT

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U.S. Cl. 96—1 R

13 Claims

ABSTRACT OF THE DISCLOSURE

Migration material in contact with an insulating layer is caused to imagerwise selectively migrate to at least locations in depth in the insulating layer by subjecting the migration material to an imagerwise migration force and then contacting the insulating layer with a molten liquid.

BACKGROUND OF THE INVENTION

This invention relates in general to imaging, and more specifically to migration imaging and a process for changing the resistance of an insulating layer to migration of migration material.

Recently, a migration imaging system capable of producing high quality images of high density, continuous tone and high resolution has been developed. Such migration imaging systems are disclosed in copending applications Ser. Nos. 837,780 and 837,591, both filed June 30, 1969 and are hereby expressly incorporated herein by reference. In a typical embodiment of the new migration imaging system, there is employed an imaging member comprising a substrate having an overlayer of softenable material. Within the softenable material, there is dispersed electrically photosensitive particles. Typically, a latent electrostatic image is formed, for example, by electrostatically charging the member and exposing it to a pattern of electromagnetic radiation to which the particles are sensitive. There is thereby formed in the imaging layer an imagerwise pattern within the particles which have a tendency to migrate toward the substrate. Upon reducing the resistance of the softenable layer to such migration, the particles migrate toward the substrate forming what is known as a migration image on or near the substrate.

One mode of developing a latent image in the migration imaging system is to contact the imaging member containing the latent image with a solvent which dissolves away 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 on the substrate while the softenable layer is washed away. The particle image may then be fixed to the substrate in a variety of ways known to those skilled in the art or transferred. For many preferred photosensitive particles, the image produced by the above process is a negative of the positive original, i.e. particles deposit in imagerwise configuration corresponding to the areas exposed to the radiation. However, positive-to-positive systems are also possible by varying imaging parameters. Those portions of the photosensitive material which do not migrate to the substrate are washed away by the solvent with the softenable layer. As disclosed in the copending applications referred to above, by means of other developing techniques, the softenable layer may at least partially remain behind on the supporting substrate with or without a relatively unmigrated pattern of marking material complementary to said migrated material.

In other imaging member embodiment, migration mate-

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rial is formed as a single layer over but in contact with the free surface of the softenable layer in a multi-layer configuration.

"Softenable" as used herein is intended to mean any material which can be rendered more permeable to migration material migrating through its bulk. Conventionally, changing permeability is accomplished by dissolving, melting and softening as by contact with heat, vapors, partial solvents and combinations thereof.

"Fracturable" layer or material as used herein, means any layer or material which is capable of breaking up during development, thereby permitting portions of said layer to migrate toward the substrate in image configuration. The fracturable layer may be particulate, semi-continuous or continuous in various embodiments of the migration imaging members.

"Contiguous" for the purpose of this invention is defined as in Webster's New Collegiate Dictionary, Second Edition, 1960; "an actual contact" touching; also, near, though not in contact; adjoining.

In certain methods of forming the latent image, non-photosensitive or inert, fracturable layers and particulate material may be used to form images, for example, wherein the softenable material is, in addition, photoconductive. The characteristics of the images produced are dependent on such process steps as charging, exposure and development as well as the particular combination of process steps. High density, continuous tone and high resolution are some of the image characteristics possible. The images are generally characterized as fixed or unfixed particulate images with or without a portion of the softenable layer and unmigrated portions of the layer left on the imaged member.

As stated above the permeability of the softenable layer is modified in several ways such as by melting the layer or by contacting the layer with solvents. While melting the layer does not effect removal, contacting the layer with solvent generally can perform the removal of the softenable layer while allowing appropriate migration material to migrate to form an image, leaving an unfixed imagerwise formation of migration material on a substrate. Of course, to use the image which has been developed by means of a solvent, one must fix the image to the substrate and in most instances it is desirable to remove the unwanted, unmigrated migration material and softenable material when the resistance to migration of the softenable layer has been modified by means of melting the softenable layer. There is herein proposed a method of imaging which both removes the unwanted, unmigrated migration material and softenable layer while leaving the migrated migration material well fixed to the substrate.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide an imaging system which provides the above noted advantages.

It is another object of this invention to provide a novel migration imaging system.

It is another object of this invention to provide a migration imaging system wherein the migration image is fixed to a substrate.

These and other objects of this invention will be apparent from the following detailed description taken in conjunction with the attached drawings. In accordance with this invention, there is provided an imaging member comprising migration material in contact with a softenable layer. The migration material is caused to imagerwise migrate to at least locations in depth in the softenable layer by subjecting the migration material to an imagerwise migration force and changing the resistance of the softenable layer to the migration of the migration material by contacting the softenable layer with a molten liquid, pref-

erably of the same material as that forming the softenable layer. In the event the molten material is different from that of the softenable layer, the temperature of the molten material must be equal to that which will soften the softenable layer to the extent necessary to modify the resistance of the softenable layer to the migration of the migration material. In the most preferred embodiment, the molten material not only alters the resistance to migration of the softenable layer to the migration of the migration material but also removes the unmigrated material and all of the softenable layer. There is thus formed in the preferred embodiment a migration image on the substrate coated over with the molten material employed to develop the image.

BRIEF DESCRIPTION OF THE DRAWINGS

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

FIG. 1 is a partially schematic drawing 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.

FIG. 2 is a perspective view of the development step.

DETAILED DESCRIPTION OF THE DRAWING

Referring now to FIG. 1A, there is shown a schematic drawing of an example of one embodiment of an imaging member 10 according to this invention comprising substrate 11, electrically insulating softenable layer 12 which has in contact with its upper surface a fracturable migration layer 13 of particulate material.

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 softenable 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 belts, 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 Du Pont, or Mylar coated with copper iodine.

Electrically insulating substrates may also be used which opens up a wide variety of film formable materials such as plastics for use as substrate 11.

Softenable layer 12, which may comprise one or more layers of softenable materials, may be any suitable material, typically a plastic or thermoplastic material and, in addition, for the optimum electrical-optical mode hereof is substantially electrically insulating during the migration force applying and softening steps hereof. It should be noted that layer 12 should preferably be substantially electrically insulating for the preferred modes hereof of applying electrical migration forces to the migration layer. More conductive materials may be used in the electrical mode hereof of applying a constant and replenishing supply of charges in image configuration. In these optimum and preferred modes, it is found that higher conductivity softenable layers 12 are accompanied by charge injection

from the substrate into layer 12 and/or by other conductively-related mechanisms which discharge layer 12 causing removal of the coulombic migrating force on the particle before migration has occurred satisfactorily.

"Softenable" as used herein to depict layer 12 is intended to mean any material which can be rendered by the developing step hereof more permeable to particles migrating through its bulk. Conventionally changing permeability is accomplished by contacting the layer with a molten liquid which melts or softens the material comprising the layer.

Typically substantially electrically insulating softenable materials include Staybelite Ester 10, a partially hydrogenated rosin ester, Foral Ester, a hydrogenated rosin triester and Neolyne 23, an alkyd resin, all from Hercules Corp.; SR type silicone resins available from General Electric Corporation; Sucrose Benzoate, Eastman Chemical; Velsicol X-37, a polystyreneolefin copolymer from Velsicol Chemical Corp.; Hydrogenated Piccopale 100, Piccopale H-2, highly branched polyolefins, Piccotex 100, a styrene-vinyl toluene copolymer, Piccolastic A-75, 100 and 125, all polystyrenes, Piccodiene 2215, a polystyreneolefin copolymer, all from Pennsylvania Industrial Chemical Corp.; Araldite 6060 and 6071, epoxy resins from Ciba Corp.; R5061A, a phenylmethyl silicone resin, from Dow Corning; Epon 1001, a bisphenol A-epichlorohydrin epoxy resin, from Shell Chemical Corp. and PS-2, PS-3, both polystyrenes and ET-693, a phenol-formaldehyde resin, from Dow Chemical; custom synthesized copolymers of styrene and hexylmethacrylate, a custom synthesized polydiphenylsiloxane; a custom synthesized polyadipate; acrylic resins available under the trademark Acryloid from Rohm & Haas Co.; and available under the trademark Lucite from E. I. du Pont de Nemours & Co.; thermoplastic resins available under the trademark Pliolite from the Goodyear Tire & Rubber Co.; a chlorinated hydrocarbon available under the trademark Aroclor from Monsanto Co.; thermoplastic polyvinyl resins available under the trademark Vinylite from Union Carbide Co.; other thermoplastics disclosed in Gunther et al. Pat. 3,196,011; waxes and blends, mixtures and copolymers thereof.

The above group of materials is not intended to be limiting, but merely illustrative of materials suitable for softenable layer 12. The softenable 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 1/2 to about 16 microns have been found to be preferred, but a uniform thickness over the imaging area from about 1 to 4 microns is found to provide for high quality images while permitting ready image member construction.

Layer 12 may be formed by any suitable method including dip coating, roll coating, gravure coating, vacuum evaporation and other techniques.

Migration layer 13, portions of which migrate towards or to the substrate during image formation under influence of the migration forces hereof, illustratively is a fracturable layer of particles. While it is preferred for images of highest resolution, density and utility that layer 13 be a fracturable layer and optimally that the fracturable material be particulate, layer 13 may comprise any continuous or semi-continuous, fracturable layer, such as a swiss cheese pattern, which is capable of breaking up into discrete particles of the size of an image element or less during the development step and permitting portions to migrate towards the substrate in image configuration.

The description and methods of preparing fracturable and non-fracturable migration layers are more fully described in copending commonly assigned application Ser. No. 837,780 referred to above which is incorporated herein by reference.

The thickness of layer 13 is preferably from about 0.01 to about 2.0 microns thick, although five micron

layers have been found to give good results for some materials.

When layer 13 comprises particles, a preferred average particle size is from about 0.01 to about 2.0 microns to yield images of optimum resolution and high density compared to migration layers having particles larger than about 2.0 microns. For optimum resultant image density the particles should not be much above about 0.7 micron in average particle size. Layers of particle 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 that layer. It should be recognized that the particles may not all be packed tightly together laterally or vertically so that some of the thickness of layer 13 may constitute softenable material.

Migration layer 13, while shown in the accompanying drawings as a localized layer in imaging member 10, may also be dispersed throughout softenable layer 12. In the dispersed or binder form, the imaging process steps of this invention are not altered and essentially the same migration material and softenable layers are employed as are described herein with respect to the layered configuration. Further descriptions and methods of preparing imaging members having migration material dispersed through the softenable layer are found in commonly assigned, copending application Ser. No. 837,591 referred to above which is incorporated by reference.

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 optically inert particles. For the modes hereof employing an electrical migration force, the migrating portions of layer 13 should be sufficiently electrically insulating to hold their electrical migration force until the desired amount of migration has occurred. Conductive particles may be used, however, 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 softenable material and otherwise not adversely reactive therewith, and in any molten liquid which may be used in the development step hereof.

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 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); 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 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, photoemission, photochemical effects and other 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 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 and organic photoconductors include cadmium sulfide, zinc oxide, cadmium selenide, cadmium yellows such as Lemon Cadmium Yellow X-2273 from Imperial Color and Chemical Dept. of Hercules Corp., azo dyes such as Watchung Red B, a barium salt of 1-(4'-methyl - 5' - chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, C. I. No. 15865, a quinacridone, Monastral Red B, both available from Du Pont; Indofast double scarlet toner, a Pyranthrone-type pigment available from Harmon Colors; Quinido-magenta RV-6803, a quinacridone-type pigment available from Harmon Colors; Cyan Blue, GTNE, the beta form of copper phthalocyanine, C. I. No. 74160, available from Collway Colors; Monolite Fast Blue GS and the alpha form of metal-free phthalocyanine, C. I. No. 74100, available from Arnold Hoffman Co. Other photoconductive materials are described in copending application Ser. No. 837,780 referred to above. 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.

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 August 30, 1965, now U.S. Pat. No. 3,656,990, and as further described herein.

It will also be appreciated that the migration 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, filed Jan. 13, 1967 now abandoned which is incorporated herein by reference.

In addition to the configuration shown in FIG. 1, with or without substrate 11, additional modifications in the basic structure such as an overcoated structure in which the migration material layer is sandwiched between two layers of softenable material may also be used. Also, multiple layers each layer comprising a migration layer on or in a softenable layer may be used, with adjacent migration layers in the tiered structure separated from each other or touching.

Also the softenable layer may comprise one or more layers of different softenable materials with, for example, the migration layer contiguous the free surface of one layer of softenable material, which is coated on a supporting softenable layer optionally on a supporting substrate. As a further variation, one of the layers of softenable material may be stable against agglomeration of the migration material and another layer unstable against agglomeration to enhance the agglomerating, background reducing effect as described in copending application Ser. No. 612,122, filed Jan. 27, 1967, now aban-

done wherein the optical transmission of the unmigrated fracturable material is greatly increased by a truly astounding agglomeration effect of the unmigrated material to substantially transparentize these portions of the imaging member.

Thus, there has been described the layered configuration migration imaging member of this invention which is separately disclosed in greater detail and claimed in copending application Ser. No. 635,256, filed May 1, 1967.

Referring now to the imaging methods of this invention and how material of the migration layer of the member described above is caused to migrate in depth in the softenable layer; broadly, the imaging methods involve applying to the migration layer material an imagewise migration force, which typically is associated with a latent imagewise change of the imaging member which modifies directly or indirectly the force of the migration layer toward the bulk of the softenable layer and typically toward a face of the softenable layer or, where a substrate is used, toward the substrate-softenable layer interface; said migration material force applying step occurring before, during or after a second step of changing the resistance of said softenable material layer to migration of migration material.

There are a variety of forces which can be applied to and be made to act on the migration layer to cause it to move in image configuration in depth in a softenable layer. Such forces include electrical or electrostatic, magnetic, gravitational and centrifugal forces. An even greater variety of ways exists in which these forces can be made to act on a migration layer either uniformly or imagewise.

Evidencing the versatility of this invention, modes of imagewise applying an imagewise migration force to migration layer material hereof include:

(a) Applying an imagewise charge to a migration layer which produces an imagewise attraction of the migration layer material to opposite polarity charges induced, by the charges originally applied on the migration layer, on the opposite face of the softenable layer or on the substrate of an imaging member;

(b) Applying an imagewise external electrical field acting on a uniformly charged migration layer;

(c) Applying a uniform external electric field acting on an imagewise charged migration layer;

(d) Applying an imagewise magnetic field acting on a uniformly magnetized migration layer.

It will be seen that the strength of an imagewise electrical or electrostatic migration force, the preferred migration force of this invention will depend upon the strength of the electric charge on or in the migration layer and the strength of any external electric field. The generation of the charge on or in the migration layer may be affected by:

(i) The distribution of the charge put on or in the structure including on or in the migration layer;

(ii) The ability of the migration layer to hold charge;

(iii) The ability of the softenable layer to hold charge;

(iv) The magnitude of the electric field through the imaging member.

Referring now more specifically to the imaging modes hereof and to FIGS. 1B and 1C, a latent image is formed by the optimum electrical-optical mode hereof in a member 10 with a layer 13 comprising photosensitive material by the preferred method comprising the steps of uniform corona charging (FIG. 1B) and imagewise exposing (FIG. 1C). In FIG. 1B, the imaging member is uniformly electrostatically charged, illustratively by means of a corona discharge device 14 which is shown to be traversing the member from left to right depositing a uniform, illustratively positive charge on the surface of layer 13. Substrate 11 if conductive is typically grounded as the device 14 traverses. For example, corona discharge devices of the general description and generally operating

as disclosed in Vyverberg Pat. 2,836,725 and Walkup Pat. 2,777,957 have been found to be excellent sources of corona useful in the charging of member 10. Corona charging is preferred because of its ease and because of the consistency and quality of 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). However, other charging techniques ranging from rubbing the member, to induction charging, for example, as described in Walkup Pat. 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 latent image, after charging, member 10 is exposed to an imagewise pattern of activating radiation 15. For purposes of illustration, the surface electrical charges are depicted as having moved into particulate layer 13 in the illuminated areas. Although this representation is speculative, it is helpful for an understanding of the present invention to consider the particles of layer 13 in illuminated areas of layer 13 to have a greater capability of accepting charge. The latent image thus formed especially from the exposure levels given below cannot readily be detected by standard electrometric techniques as an electrostatic image, for example, as found in xerography and as found in the preferred process mode hereof, so that no readily detectable change in the electrostatic or coulombic force is found after exposure although when layer 12 is softened the latent image formed as a result of the charging and exposing steps selectively in image configuration causes the particles to migrate.

Any suitable exposure level may be used. Exposures for optimum quality images will depend on many factors including the composition of photosensitive migration layer 13. Illustratively, for amorphous selenium migration layers, 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 100 f.c.s. may be preferred for photosensitive migration layers of composition other than the preferred materials comprising amorphous selenium. Lower exposures such as about ½ f.c.s. may be used for photosensitive migration layers comprising certain phthalocyanines.

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

Uniform exposure or no exposure with uniform softening and uniform migration layer 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 in-

candescent lamps, X-rays, beams of charged particles, infrared, ultra violet and so forth. The imagewise exposures may be before, during or after charging and before or during developing of the softenable layer, wherein the photosensitivity employed is permanent, persistent or temporary. Also, the latent image may result from the heating effects of the incident radiation pattern, either on the softenable layer or the migration layer to produce an imagewise change in conductivity thereby producing an electrical migration force pattern. The above described process embodiment of the electrical-optical imaging mode hereof is preferred because of its simplicity, versatility and because of the high quality images produced.

An alternative imaging member construction which may be used with the above described method steps in the optimum electrical-optical mode hereof is to use a member comprising a photosensitive softenable layer and a migration layer of a material which need not be photosensitive, as more fully described in copending application Ser. No. 553,837, filed May 31, 1966, now abandoned.

A variation of the electrical-optical mode is to imagewise heat radiate in the exposure step a thermoconductive softenable layer and/or migration layer, 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 or change may occur subsequently in the layer 12 softening step hereof.

According to a preferred process embodiment of the preferred electrical migration force modes hereof, a latent electrostatic image of a type similar to those found in xerography is placed in or on the imaging member 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 Pat. 2,982,647 and Walkup Pats. 2,825,814 and 2,937,943;

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

(iv) Electron beam recording techniques, for example, as described in Glenn Pat. 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 thereof, 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 Pat. 3,057,997.

The magnitude of the electrostatic latent image applied in this particular mode of forming a latent 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 insure 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.

The next step of this invention is developing i.e., rendering the softenable layer sufficiently permeable to mi-

gration of migration material to permit migration or to permit what is often a latent imaged member after the migration force applying step hereof to become visibly (or detectable by other means) imaged. This imaged effect is produced by layer 13 imagewise migrating in depth into the bulk of layer 12. Developing can include both the softening of the softenable layer and the removal of unmigrated migration material. Developing is the mechanism which permits selected portions of the migration layer to imagewise migrate to locations in depth in the softenable layer, or to the substrate while the remaining migration material may remain substantially unmigrated in or on the softenable layer or migrate a shorter distance in the softenable material or be washed away in the wash away mode of development.

As shown in FIG. 2 the development step in accordance with the process of this invention involves the contacting of an imaging member of this invention with a molten liquid, preferably comprising the same material as that of the softenable layer of the imaging member. Accordingly, in FIG. 2 imaging member 10 is shown being withdrawn from vessel 20 containing molten liquid 21. Residing on imaging member 10 is image 22 formed by the migration or migration material to the substrate and made visible by the removal in the molten liquid of unmigrated migration material. In instances wherein the molten liquid is a thermoplastic resin, it is found that image 22 is overcoated with a thin layer of the thermoplastic, thus providing a fixed image on imaging member 10. The amount of time required for development by this means is usually very short and in the order of one second or less. However, longer periods of development time can be employed as the migrated material adheres to the imaging member and is not easily removed by the molten liquid. Therefore, the development time is not critical.

As stated above it is preferred that the molten liquid be of the same composition as that of the softenable layer. However, in the event that a material dissimilar to the softenable layer is employed, it is understood that such material must remain molten at a temperature which is at least the softening temperature for the softenable layer so as to permit imagewise migration of the migration material. Hence, the materials mentioned above as being usable in the softenable layer, can also be employed as molten liquid 21 by maintaining the material in the molten state. In addition to those materials mentioned above for use in the softenable layer of imaging member 10, microcrystalline waxes can be employed such as Sunoco 1290, Sunoco 5825 and Sunoco 985 all available from the Sun Oil Company; Parafint RG available from the Moore and Munger Company; paraffin waxes such as Sunoco 5512, Sunoco 3425 available from the Sun Oil Company; Sohio Parowax available from the Standard Oil Company; waxes made from hydrogenated oils such as Capitol City 1380 wax available from the Capitol City Products Company, Columbus, Ohio; Caster Wax L-2790, available from the Baker Caster Oil Company; and Vitekote L-304 available from Duro Commodities. However, the thermoplastic materials listed above are preferred.

As mentioned above dissimilar materials can be used as the molten liquid and as the material for softenable layer 12 in imaging member 10. Thus, for example, softenable layer 12 can comprise one of the waxes listed above while molten liquid 21 can be a thermoplastic material maintained at a temperature which is above the softening temperature of the wax so as to permit migration of the migration material. The resultant image will have a durable thermoplastic coating over its surface which surface tends to protect as well as to fix the image to the substrate.

In addition to lowering the resistance of softenable layer 12 to migration of migration material 13, molten liquid 21 serves to wash away unmigrated material 13 and at least a portion of softenable layer 12. As with the

material useful in the softenable layer, molten liquid 21 is sufficiently insulating so as not to dissipate the electrical charges on the imaging member prior to the migration of the migration material. However, in the event that the migration material has been allowed to migrate prior to the introduction of the imaging member into the molten liquid, the molten liquid need not possess electrical insulation properties.

In addition to the immersion method illustrated in FIG. 2, a small amount of molten material may be employed over the surface of the softenable layer followed immediately by removal of the top surface of the softenable layer which has been contacted by the molten liquid. Other methods of applying the molten liquid will be obvious to those skilled in the art. Thus flow coating, roll coating and spraying can be employed to contact the imaging member with the molten liquid.

The following examples further specifically define the present invention. The parts and percentages are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of the migration in depth imaging system of this invention and are not intended as limitations thereof.

EXAMPLE I

An imaging member such as that illustrated in FIG. 1 is prepared by first dissolving about 5 parts of Staybelite Ester 10 in about 20 parts cyclohexanone and about 75 parts toluene. Using a gravure roller, the solution is then roll coated onto about a 3 mil Mylar polyester film having a thin semi-transparent aluminum overcoating. The coating is applied so that when air dried for about 2 hours to allow for evaporation of the cyclohexanone and toluene solvent, about a two micron layer of Staybelite Ester is formed on the aluminized Mylar. A thin layer of particulate zinc oxide dyed with Rhodamine B is formed over the Staybelite layer by cascading the zinc oxide particles on carrier beads over the surface of the layer in accordance with the procedure of Example I of copending application Ser. No. 853,869 filed Aug. 8, 1969 which is incorporated herein by reference.

The member is then migration imaged according to this invention by charging it under dark room conditions to a negative potential of about 150 volts through the use of a corona charging device such as that set forth in Walkup Pat. U.S. 2,777,957. The film is then exposed to an optical image, the exposure at about 11.2 f.c.s. in the illuminated areas. The film is then developed, i.e. softened, while still maintaining dark room conditions by immersing it in a bath of Staybelite Ester 10 maintained at a temperature of about 150° C. A migration image is formed on the imaging member and is viewed while in the bath.

EXAMPLE II

An imaging member according to Example I is charged and imaged in accordance with the procedure of Example I and is developed by dipping the charged and imaged film into a bath of molten paraffin maintained at a temperature of 55° C. for a few seconds. The image obtained on the film when removed from the liquid paraffin consists of selenium particles migrated to the film base and a coating of paraffin over the whole film base. The unmigrated selenium particles are washed away with the Staybelite Ester layer in the molten paraffin.

EXAMPLE III

An imaging member is prepared by roll coating a sheet of aluminized Mylar with an embedding wax with a melting point in the range of from about 55° C. available from the Will Scientific Company to a finished thickness of about 2 microns. The free surface of the wax layer is then embedded with a mixture of air spun graphite particles, Type 200-19 available from the Joseph Dixon Crucible Company by cascading a mixture consisting of said particles and 50 micron diameter glass beads across the sur-

face of the wax layer to form a layer of graphite about 1 micron in thickness. An electrostatic image is applied to the plate by means of a corona discharge device through a stencil as more particularly described in copending application Ser. No. 483,675 filed Aug. 30, 1965 which is incorporated herein by reference. The image areas are thus negatively charged to about 200 volts. The thus charged imaging member is then immersed in a reservoir of molten paraffin of the same kind as coated on the aluminized Mylar which is maintained at a temperature of 55° C. Upon removal of the imaging member, there is found an image on the film consisting of graphite deposited according to the charge pattern and a coating of paraffin over the entire film base. The graphite particles in the uncharged areas were washed away with the matrix layer.

EXAMPLE IV

A pigment binder dispersion employing as the pigment the X-form metal-free phthalocyanine prepared as described in U.S. Pat. 3,357,989. The binder comprises a mixture of equal weight amounts of a hydrocarbon wax available under the tradename Sohio Parowax (melting point 35°-56° C.) from the Standard Oil Company and a modified styrene polymer available under the tradename Piccolastic A-50 from Pennsylvania Industrial Chemical Co. The dispersion is prepared by combining a dry weight ratio of pigment to binder of about 1 to 3 and agitating the mixture to obtain a uniform dispersion. The pigment binder dispersion is coated over a Mylar film forming a dried migration layer of about 2 microns in thickness.

An imagewise migration force is applied to the member by uniformly electrostatically charging the member to a positive surface potential of about 4,000 volts using a single sided corona charging device employing a grounded plate under the Mylar film. The charged film is then contact exposed to a positive transparency at an intensity of about 0.10 foot-candle seconds in the exposed areas. The charged and imaged member is then immersed in a reservoir of an equal weight mixture of Sohio Parowax and Piccolastic A-50 and heated to about 90° C. to cause migration in the unexposed areas while substantially no migration occurs in the exposed areas. There is thus produced an image configuration of migrated phthalocyanine particles on the Mylar film while the unmigrated phthalocyanine particles together with the binder is washed away in the reservoir. Upon removal of the imaging member, an image coated with a mixture of Parowax and Piccolastic A-50 remains on the Mylar film.

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 migration material in contact with a softenable layer on a substrate;
- (b) applying an electrical imagewise migration force to said migration material;
- (c) contacting said softenable layer with a substantially electrically insulating molten liquid, said molten liquid becoming molten at a temperature greater than ambient temperature but below a temperature at which degradation occurs to the imaging member, thereby reducing the resistance to migration of said migration material in depth in said softenable layer

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whereby said migration material migrates in image-wise configuration in depth through said softenable layer toward said substrate, and said softenable layer containing said unmigrated migration material is at least partially removed; and

(d) then reducing said molten liquid to ambient temperature thereby forming a solid coating over the migration imaged member formed by step (c).

2. The method of claim 1 wherein said substrate is electrically conductive.

3. The method of claim 1 wherein the migrating material is particulate material having an average particle size in the range of from about 0.01 to about 2.0 microns.

4. The imaging method of claim 1 wherein the average size is in the range of from about 0.01 to about 0.7 micron and wherein said softenable layer is from about one half to about 16 microns.

5. The method of claim 1 wherein said migration material is electrically photosensitive.

6. The method of claim 1 wherein the molten liquid and the softenable layer are comprised of the same material.

7. The method of claim 1 wherein the molten liquid and the softenable layer are comprised of dissimilar materials.

8. The method of claim 5 wherein said migration material comprises selenium.

9. The method of claim 5 wherein said migration material comprises phthalocyanine.

10. An imaging method comprising the steps of:

(a) providing an imaging member comprising a layer of electrically photosensitive migration material spaced apart from at least one surface of but contacting a softenable layer;

(b) electrostatically charging said softenable layer;

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(c) exposing said migration material to an imagewise pattern of electromagnetic radiation to which said migration material is sensitive;

(d) while said softenable layer is in contact with a substrate contacting said softenable layer with a substantially electrically insulating molten liquid, said molten liquid becoming molten at a temperature greater than ambient temperature but below a temperature at which degradation occurs to the imaging member, thereby reducing the resistance of said softenable layer to migration of said migration material whereby said migration material migrates in imagewise configuration to said substrate and said softenable layer containing said unmigrated migration material is at least partially removed; and

(e) then reducing said molten liquid to ambient temperature thereby forming a solid coating over the migration imaged member formed by step (c).

11. The method of claim 10 wherein said migration material comprises selenium.

12. The method of claim 10 wherein said molten liquid and said softenable layer are comprised of the same material.

13. The method of claim 10 wherein said molten liquid and said softenable layer are comprised of dissimilar materials.

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