United States Patent [19]

Goffe

[11] **3,723,113**

[45] **Mar. 27, 1973**

[54] POLYCHROMATIC ELECTROSOLOGRAPHIC IMAGING PROCESS

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[22] Filed: **Nov. 9, 1970**

[21] Appl. No.: **87,666**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 609,056, Jan. 13, 1967, abandoned.

[52] **U.S. Cl.** ....**96/1.2**, 96/1 R, 96/1.4, 117/1.7, 117/17.5 LE

[51] **Int. Cl.**.....**G03g 13/04**, G03g 13/06, G03g 13/22

[58] **Field of Search** 204/181; 96/1, 1.2, 1.5; 252/501; 117/17.5

[56] **References Cited**

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3,515,549	6/1970	Bixby	96/1.5
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[57] ABSTRACT

A polychromatic migration imaging system is disclosed. Typically, a plate of a conductive substrate coated with a softenable insulating layer overcoated with a mixture of different colored photosensitive particles is electrostatically charged, and exposed to a polychromatic image. The softenable layer is softened, allowing selective migration of some particles to the substrate, resulting in a polychromatic image.

14 Claims, 6 Drawing Figures

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3,723,113

SHEET 1 OF 2

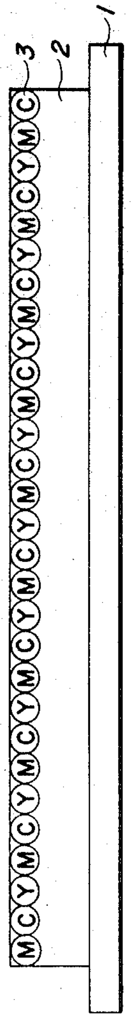

FIG. 1

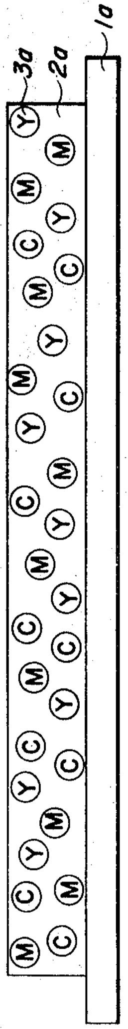

FIG. 1a

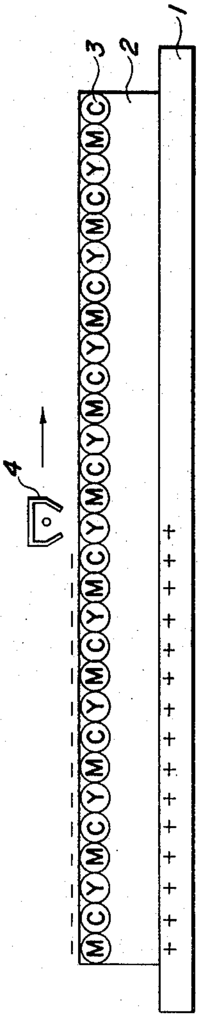

FIG. 2

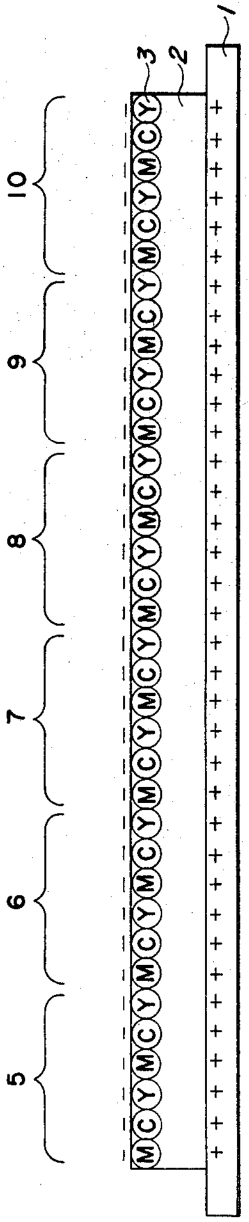

FIG. 3

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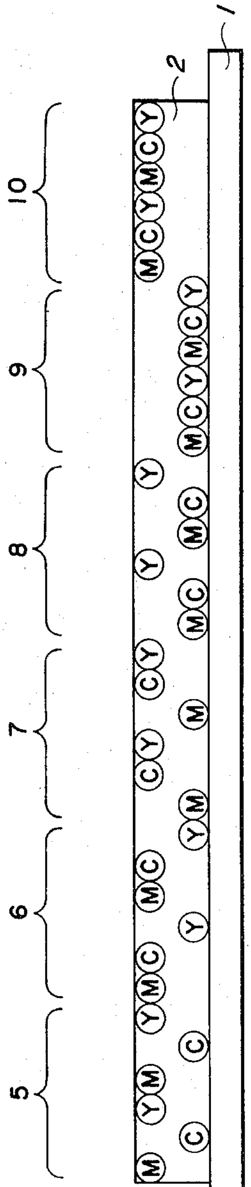

FIG. 4

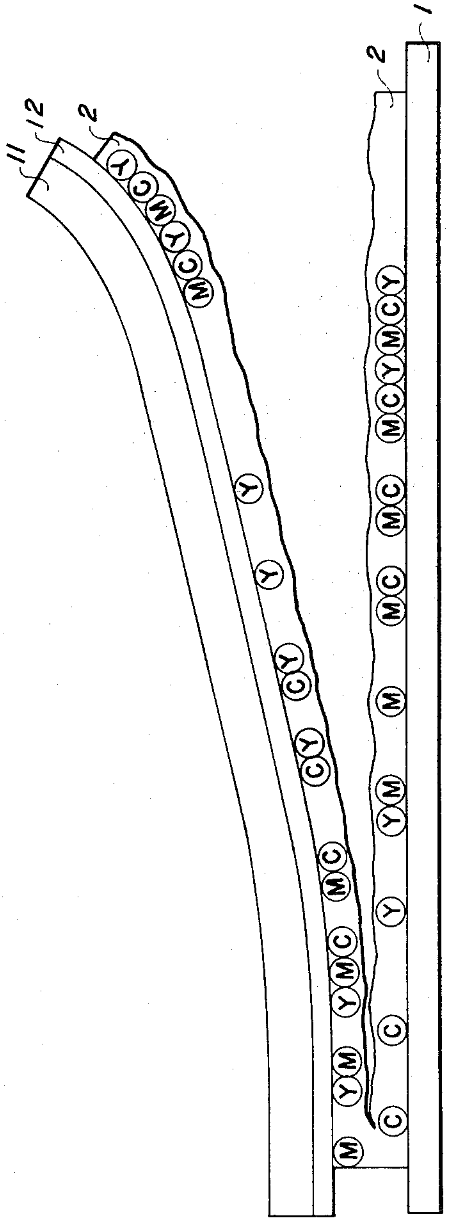

FIG. 5

POLYCHROMATIC ELECTROSOLOGRAPHIC IMAGING PROCESS

This application is a continuation-in-part of my copending application Ser. No. 609,056 filed Jan. 13, 1967, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates in general to migration imaging systems, and more specifically, concerns a polychromatic migration imaging system.

There has been recently developed a migration imaging system heretofore referred to as a graphic imaging system capable of producing images of high quality and excellent resolution. This system is described in detail and claimed in copending applications Ser. Nos. 837,591 and 837,780, both filed June 30, 1969, both of which applications are expressly incorporated herein by reference. In a typical embodiment of this imaging system, an imageable plate is prepared by coating a layer of a softenable material onto conductive substrate and overcoating said softenable material with a particulate electrically photosensitive layer. The fracturable layer may be particulate and the softenable layer may be soluble in a solvent which does not attack the fracturable layer. An electrostatic latent image is formed on the surface of the fracturable layer, e.g., by uniform electrostatic charging of the surface and exposure to a pattern of activating electromagnetic radiation. The softenable layer is then softened, e.g., by dipping the plate in a solvent. Portions of the particulate layer which have retained or accept a surface electrostatic charge migrate through the softenable layer as it is softened or dissolved leaving an image on the conductive substrate conforming to a negative of the original. Those portions of the fracturable layer which do not migrate to the conductive substrate and the softenable layer may be washed away with a solvent for the softenable layer. The image resulting is of high quality and of a specially high resolution. Alternative embodiments are further described in the above cited copending applications.

As described in the above cited copending applications a variety of electrically photosensitive material may be used in the fracturable layer. In each case, however, particles of a single material are used producing monochromatic images corresponding to the original. For many uses, e.g., copying of ordinary type written or printed material, a monochromatic image is entirely suitable. However, where the original to be copied is in two or more colors it would be desirable to produce copies in multiple colors.

Various processes for producing polychromatic copies of an original are known in the imaging art. Several of these processes are in extensive commercial use. Probably, the four most widely used photographic multicolor imaging processes are: (1) the diffusion transfer color process, (2) the process utilizing color separation negatives, (3) the process utilizing complementary full color negatives for producing positive prints and (4) the reversal process giving positive full color-images.

The diffusion transfer color process is described in a number of patents, for example, U.S. Pat. No. 3,161,506 and British Pat. No. 804,971. Typically, photographic elements containing silver halide emulsion layers and layers containing diffusible dye developers are exposed to an original to record a latent image in the silver halide layer. This is then treated with an alkaline processing composition which permeates the emulsion layers and layers containing the dye developers which then develop the latent images to silver images. At the same time, oxidation products of the dye developers are formed in situ with the silver images. These are relatively non-diffusing in the colloid vehicle of the layers. The residual unoxidized dye developers remaining in the layers in imagewise 4 distribution are transferred by diffusion to a superposed reception element substantially to the exclusion of the silver image and the oxidized dye developer to provide a positive dye image.

Where an element containing differentially sensitized silver halide emulsion layers is used and subtractively colored dye developers are present in or contiguous to the respective emulsion layers, upon treatment with the processing liquid, the dye developers are oxidized and rendered non-diffusing in the developed regions of the layers and the residual dye developer images in the positive regions are transferred by diffusion and in register to the reception element to provide a multicolor reproduction.

When carefully performed, this process is capable of producing images of excellent quality. However, the development process is rather complex, utilizing various chemical developing agents and must be performed with great care. Further, the dyes used are sensitive to adverse conditions of temperature and humidity which may produce undesirable shifts in color balance with time and may decrease the density of the final image.

In the process utilizing separation negatives, several negatives are made of the original to be reproduced by exposure through different suitable colored filters. Then, a single silver halide emulsion layer is sequentially exposed to the properly registered separation negatives, the emulsion layer being developed after each exposure with a color-forming developer to form the dye-image in the silver image. The silver image is re-halogenated after each development and finally all silver and silver salts are removed from the emulsion. Such processes are described, for example, in U.S. Pat. Nos. 2,333,359 and 2,443,909.

This process is capable of producing color images of high density and good resolution and color balance. However, where the plural separation negatives are made sequentially in a single camera, the object photographed must be stationary throughout the period of multiple exposure. If the object to be photographed is not stationary, a complex camera holding several negatives and utilizing beam splitters to direct portions of the light to each negative must be used. Also, the development steps in producing the final color image are many and complex.

Systems utilizing single complementary negatives or reversal films are similar in that each uses a complex, multilayer emulsion containing sub-layers each sensitive to light of a different color. A typical film includes a transparent base having an anti-halation layer on the rear surface and coated with three emulsions sensitive, respectively, to yellow, green and red light. Between these selectively sensitive layers are filter layers which prevent undesired light from passing to the lower layers. A negative film produces a final image in colors complimentary to the original. This may then be used for the printing of positive prints with a similar emulsion. Reversal films produce an image in colors corresponding to those of the original. These films, with their many thin layers, are difficult and expensive to coat. The dyes used are not entirely stable and may fade or change color with exposure to light and heat. These films tend to have very small exposure latitude. These films, however, are capable of producing images of good color quantities and high resolution and are easily exposed in a conventional camera.

While the photographic multi-color imaging processes generally in use today are capable of producing images of excellent quality, the processes are often cumbersome and complex in the exposure or the developing processes or both, and the final images are often subject to degradation under adverse conditions of temperature and humidity. Therefore, there is a continuing need for improved photographic multi-color imaging processes and materials having the inherent simplicity of the photoelectro-solographic system described above.

SUMMARY OF THE INVENTION

It is therefore, an object of this invention to provide a photographic multi-color imaging process devoid of the above noted deficiencies.

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

It is another object of this invention to provide a material for producing polychromatic images which is highly resistant to degradation due to the exposure to light, heat of high humidity.

It is another object of this invention to provide a simple migration imaging plate capable of producing polychromatic images.

The above objects and others are accomplished by providing an imaging system utilizing an imageable plate which comprises a layer of softenable material having dispersed therethrough or coated on the surface thereof a non-imagewise mixture of electrically photosensitive particles of at least two colors. Alteratively, the softenable layer may be coated on a thin electrically insulating or conductive substrate. In the configuration, with the insulating substrate, higher fields would be used across the softenable layer. The particles of each color responds to light of a different color so that a polychromatic image will be formed from a polychromatic original. Typically, an image may be formed on the above described plate by uniformly electrostatically charging the surface of the plate and exposing the plate to a polychromatic image. The image is developed by decreasing the resistance to migration of the photosensitive particles through the softenable layer to allow (or cause) imagewise migration of particles through the softenable layer. Most commonly, the softenable layer is softened as by heat or solvent contact. The softenable layer can be softened as by dipping the plate in a solvent for said softenable layer. Particles which have been struck by light of an appropriate color migrate to the substrate leaving behind unexposed particles. An image is thus formed on the substrate corresponding to a positive or a negative of the original, depending upon process variables.

In such a polychromatic system, the particles are selected so that those of different colors respond to different wavelengths in the visible spectrum corresponding to their principal absorption bands. The pigments should be selected so that their spectral response curves do not have substantial overlap, thus allowing for color separation and substantial multi-color image formation. In a typical multi-color system, the particle dispersion should include cyan colored particles sensitive mainly to red light, magenta colored particles sensitive mainly to green light, and yellow colored particles sensitive mainly to blue light. When mixed together and coated on the surface of the softenable layer, or dispersed throughout the softenable layer these particles produce a black appearing layer. These particles perform the dual function of final image colorant and photosensitive medium.

The particles may comprise any suitable material having the desired spectral and photosensitive characteristics.

Any suitable photosensitive particles may be used in carrying out the invention, regardless of whether the particular particle selected is organic, inorganic and is made up of one or more components in solid solution or dispersed one in the other or whether the particles are made up of multiple layers of different materials. Typical photosensitive particles include organic particles such as 8,13,-dioxodinaphtho-(1,2,2′,3′)-furan-6-carbox-p-methoxyanilide; Locarno Red, C.I. No. 15865, 1-(4′-methyl-5′-chloroazobenzene-2′sulfonic acid)-2-hydroxy-3-naphthoic acid; Watchung Red B, the barium salt of 1-(4′methyl-5′-chloroazobenzene-2′ -sulfonic acid)-2-hydroxy-3-naphthoic acid, C.I. No. 15865; Naphthol Red B, 1-(2′-methoxy-5′-nitrophenylazo)-2-hydroxy-3″-nitro-3-naphthanilide, C.I. No. 12355; Duol Carmine, the calcium lake of 1-(4′-methylazobenzene-2′-sulfonic acid)-2-hydroxy-3-naphthoic acid, C.I. No. 15850; Calcium Lithol Red, the calcium lake of 1-(2′-azonaphthalene-1′-sulfonic acid)-2-naphthol, C.I. No. 15630; Quinacridone and substituted quinacridones such as 2,9-dimethylquinacridone; Pyranthrones; Indofast Brilliant Scarlet Toner, 3,4,9,10-bis(N,N′-(p-methoxy-phenyl)-imido)-perylene, C.I. No. 71140; dichloro thioindigo; Pyrazolone Red B Toner, C.I. No. 21120; phthalocyanines including substituted and unsubstituted metal and metal-free phthalocyanines such as copper phthalocyanine, magnesium phthalocyanine, metal-free phthalocyanine, polychloro substituted phthalocyanine etc.; Methyl Violet, a phosphotung-stomolybdic lake of triphenylmethane dye, C.I. No. 42535; Indofast Violet lake, dichloro-9,18-isoviolanthrone, C.I. No. 60010; Diane Blue, 3,3′-methoxy-4,4′-diphenyl-bis(1″-azo-2″-hydroxy-3″-naphthanilide, C.I. No. 21180; Indanthrene Brilliant Orange R.K., 4, 10-dibromo-6,12-anthanthrone, C.I. No. 59300; Algol Yellow G.C., 1,2,5,6-di(C,C′-diphenyl-)-thiazole-anthraquinone, C.I. No. 67300; Flavanthrone; Indofast Orange Toner, C.I. No. 71105; 1-cyano-2, 3-phthaloyl-7,8-benzo-pyrrocoline and many other thio indigos, acetoacetic arylides, anthraquinones, perinones, perylenes, dioxazines, quinacridones, azos, diazos, thoazines, azines and the like; inorganics such as cadmium sulfide, cadmium sulfoselenide, zinc oxide, zinc sulfide, sulphur selenium, mecuric sulfide, lead oxide, lead sulfide, cadmium selenide, titanium dioxide, indium trioxide, and the like. In addition to the aforementioned pigments other organic materials which may be employed in the particles include polyvinylcarbazole; 2,3,-bis(4,4′-diethyl-aminophenyl)-1,3,4-oxidiazole; N-isopropylcarbazole; polyvinylanthracene; triphenylpyrrol; 4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinone; 4.5-diphenylimidazolidinethione; 4,5-bis-(4′-amino-phenyl)-imidazolidinone; 1,2,5,6-tetraazacyclo-octate-traene-(2,4,6,8); 3,4,-di-(4′-methoxyphenyl)-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8); 3,4-di(4′-phenoxyphenyl)-7,8-diphenyl-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8; 3,4,7,8 **-tetramethoxy**-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8); 2-mercapto-benzthiazole; 2-phenyl-4-alpha-naphthylidene-oxazolone; 2-phenyl-4-diphenylidene-oxazolone; 2-phenyl-4-p-methoxybenzylidene-oxazolone; 6-hydroxy-2-phenyl(p-dimethyl-amino phenyl)-benzofurane; 6-hydroxy2,3,-di(p-methoxyphenyl)-benzofurane; 2,3,5,6-tetra-(p-methoxyphenyl-furo-(3,2f)-benzofurane; 4-dimethylamine-benzylidene-benzhydrazide; 4-dimethyl-amino-benzylideneisonicotinic acid hydrazide; turfurylidene-(2)-4′-dimethylamino-benzhydrazide; 5-benzilidene-amino-acenaphthaene-3-benzylidene-amino-carbazole; (4-N,N-dimethylamino-benzylidene)-p-N,N-dimethylaminoaniline; (2-nitro-benzylidene)-p-bromo-aniline; N,N-dimethyl-N′-(2-nitro-4-cyano-benzylidene)-p-phenylene-diamine; 2,4-diphenyl-quinazoline; 2-(4′-amino-phenyl)-4-phenylquinazoline; 2 -phenyl-4-(4′-di-methyl-amino-phenyl)-7-methoxyquinazoline; 1,3-diphenyl-tetrahydroimidazole; 1,3-di-(4′-chlorophenyl)-tetrahydroimidazole; 1,3,-diphenyl-2-4′-dimethyl aminophenyl)-tetra-hydroimidazole; 1,3,-di-(p-tolyl)-2-[quinolyl-(2′-)]-tetrahydroimidazole; 3-(4′-dimethylaminophenyl)-5-(4″-methoxy-phenyl)-6-phenyl1,2,4-triazene; 3-pyridil-(4′)-5-(4″-dimethylaminophenyl)-6-phenyl-1,2,4-triazine; 3-(4′-amino-phenyl)-5,6-di-phenyl-1,2,4-triazene; 2,5-bis [4′ -amino-phenyl-(1′)] -1,3,3-triazole; 2,5-bis [4′-(N-ethyl-N-acetyl-amino)-phenyl-(1′)] -1,3,4-triazole; 1,5-diphenyl-3-methyl-pyrazoline; 1,3,4,5-tetraphenyl-pyrazoline; 1-phenyl-3-(p-methoxy styrl)-5-(p-methoxy-phenyl)-pyrazoline; 1-methyl-2-(3′,4′-dihydroxy-methylene-phenyl)-benzimidazole; 2-(4′-dimethylamino phenyl)-benzoxazole; 2-(4′-methoxyphenyl)-benzthiazole; 2,5-bis- [p-amine-phenyl-(1)] -1,3,4-oxidiazole; 4,5-diphenylimidazolone; 3-amino-carbazole; copolymers and mixtures thereof.

Other materials 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 2,4,7trinitro-9-fluorenone; 2,4,5,7-tetranitro-9fluorenone; 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 acid, such as acetic acid and maleic acid, succinic acid, citroconic acid, sulphonic acid, such as 4-toluene sulphonic acid and mixtures thereof.

It is to be noted that many of the above materials may be further sensitized by the charge transfer complexing technique and that many of these materials may be dye-sensitized to narrow, broaden or heighten their spectral response curves.

As stated above, any suitable particle structure may be employed. The particles should be substantially insoluble in the matrix material and in the solvent used to develop the plate after exposure. 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 action in an outer layer or a fusible or solvent softenable core of resin or a core of liquid such as dye or other marking material or a core of one photosensitive material coated with an 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 but which are not required include those described in U.S. Pat. No. 2,940,847 to Kaprelian.

A preferred average particle size of the electrically photosensitive particles is in the range of 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 microns 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 the 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.

The softenable layer may comprise any suitable material which is softenable, such as by heat or solvent application, so as to permit selective migration of portions of the particles to the substrate. Where the softenable layer is to be dissolved away either during or after imaging it should be soluble in a solvent which does not attack the particles. Typical softenable materials include polyolefins such as polyethylene and polypropylene; vinyl and vinylidene resins such as polymethylmethacrylate and polyvinylcarbazole; polyamides; polyurethanes; polypeptides; polysulfides; polycarbonates; cellulosic polymers, polysulfones; phenolic resins; amino resins; epoxy resins; silicone resins; and mixtures and copolymers thereof. Other suitable materials are described in copending applications Ser. Nos. 837,591 and 837,780. The softenable layer may have any suitable thickness. Excellent results have been obtained with layers having a thickness of about 1 to 4 microns. Therefore, this range is preferred.

The substrate may comprise any suitably electrically conductive or electrically insulating material. Typical conductive materials include metals such as aluminum, brass, stainless steel, copper, nickel, zinc; conductively coated glass such as tin oxide or indium oxide coated glass; similar coatings on plastic substrates; 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. In another particularly preferred embodiment of this invention, an imaging member comprises a softenable layer having photosensitive material dispersed therein and the softenable layer is coated directly onto a substrate which is a dielectric or non-conductive support member. Any dielectric or insulating material is suitable for the substrate in this embodiment of the invention, for example, Mylar polyester film, available from E.I. DuPont de Nemours and Co. Inc. Normally, the dielectric substrate has a thickness of up to about 3 mils. Any other insulating material compatible with the other materials used and suitable in the process steps of the inventive system may be used as the insulating substrate. For example, films of polyethylene terephthalate, polycarbonate, polysulfone, polyphenylene oxide, cellulose acetate, cellulose triacetate, cellulose nitrate, vinyl chloride, vinyl acetate, acrylic esters such as methyl methacrylate, vinyl butyral, vinyl formal, polyvinylcarbazole, rubber, chlorinated rubber, acrylonitrile resin, rubber, polyamides, polyimides, coated and impregnated materials such as wax paper, shellac coated cloth, epoxy impregnated cloths, glass, fibrous glass cloth and combinations thereof. The substrate may be opaque or transparent, depending upon the way in which the finally imaged member is to be imaged and viewed.

Imaging methods employing an insulating substrate in accordance with this invention are essentially the same as those employed herein with imaging members having the conductive substrate by additionally placing the insulating substrate of this invention in contact with a conductive member, typically grounded, and then creating the imagewise migration force across the imaging member as, for example, by charging with a corona discharge device. Alternatively, others methods known in the art for charging xerographic plates having insulating backings may also be applied. For example, the imaging member having the insulating substrate may be moved between two corona discharge devices thereby simultaneously charging both surfaces to opposite potentials. The last described method is often referred to as "double-sided charging." 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.

BRIEF DESCRIPTION OF DRAWINGS

The polychromatic migration imaging system of this invention may be further understood upon reference to the drawings, wherein:

FIG. 1 schematically shows a section through a migration imaging plate before imaging wherein the migration material is in a layer configuration.

FIG. 1A schematically shows a section through a migration imaging plate before imaging wherein the migration material is in a dispersed or binder configuration.

FIG. 2 schematically shows the electrostatic charging of the plate of FIG. 1.

FIG. 3 shows the exposure of the plate of FIG. 1 to a polychromatic image.

FIG. 4 schematically shows the development of the electrostatic latent image on the plate, and

FIG. 5 schematically shows the adhesive strip-off of the positive polychromatic image.

Referring now to FIG. 1, there is shown a schematic cross-sectional view of an example of one embodiment of the migration imaging plate of this invention. In this exemplary instance, the conductive substrate **1** comprises NESA glass (partially transparent tin oxide coated glass available from Pittsburgh Plate Glass Company). Coated over the surface of conductive substrate **1** is a softenable layer **2** comprising, for example, an organic polymeric material. On the surface of softenable layer **2** is a layer of colored photosensitive particles **3**. In a two-color system, particles of two different colors each sensitive to a different color of light would be used in layer **3**. Where it is desired to reproduce full color images, layer **3** may comprise particles of three or more different colors. Typically, in a substractive color system, the particles will be cyan, magenta and yellow in color.

In the embodiment shown in FIG. **1**, the imaging particles comprise cyan, magenta and yellow photosensitive particles. The size of the individual particles is, of course, greatly exaggerated for clarity. The particles may be embedded in the softenable layer or distributed therethrough; if desired.

FIG. **1A** schematically shows a cross-sectional view of an example of another embodiment of the migration imaging plate of this invention. In this instance, substrate **1A** comprises either an electrically insulating or electrically conductive substrate having coated thereon a softenable layer **2A** which layer has dispersed therein colored photosensitive particles **3A**. As in FIG. **1**, the particles may be of two or three or more different colors, each color sensitive to a different color of light. As above, to obtain full color imaging in the substractive color systems, the particles will be cyan, magenta and yellow in color.

FIG. **2** schematically shows the uniform electrostatic charging of particle layer **3** by means of corona unit **4**. Where desired, the particle layer **3** may be charged to either a negative or a positive potential.

FIG. **3** shows the exposure of particle layer **3** to polychromatic light. For purposes of illustration, each area across the surface of particle layer **3** is exposed to light of a different color as follows: area **5** is exposed to red light, area **6** is exposed to blue light, area **7** is exposed to green light, area **8** is exposed to yellow light, area **9** is exposed to white light, and area **10** is exposed to no light. Since these particles are electrically photosensitive, they become conductive when struck by light which they are capable of absorbing. Thus, for example, in area **5**, red light is absorbed only by the cyan particles which particles then become charge receptive. The magenta and yellow particles not absorbing the red light do not become charge receptive. In the binder structure of FIG. **1A** the photosensitive particles are not closely packed so as to prevent charge transfer between particles.

The latent electrostatic image may be developed by softening the softenable layer **2** as schematically shown in FIG. **4**. Typically, this may be done by subjecting the plate to vapors of a solvent for softenable layer **2**. Migration of particles takes place in an image configuration through the softened layer. Upon completion of the development step, the plate would appear as shown schematically in FIG. **4**. Those particles which were struck by light which they were capable of absorbing have migrated to the conductive substrate while those particles which retained a surface charge remain at or near the surface of softenable layer **2**. Since in this embodiment a subtractive image is formed, the particles remaining on the surface of softenable layer **2** form a polychromatic image corresponding to the original. Thus, in area **5** which was struck by red light, magenta and yellow particles remain which combine to form a red appearing area. Similarly, in area **6** which was struck by blue light, magenta and cyan particles remain producing a blue appearing area. Area **7** which was struck by green light has cyan and yellow particles remaining at the surface which combine to appear green. In area **8** which was struck by yellow light, both magenta and cyan particles migrate leaving behind only the yellow particles. Since the white light which struck area **9** includes colors of light absorbed by all of the particles, all particles migrate to the substrate leaving no particles at the surface. Area **10**, which was not exposed to light shows no particles having migrated. Similar results are obtained with the dispersed or binder configuration of FIG. **1A**. The positive image at the surface of softenable layer **2** is preferably treated to eliminate interference from the migrated particles on the conductive substrate. Typically, while softenable layer **2** is relatively soft and fragile a transparent sheet **11** having a pressure sensitive adhesive **12** thereon such as "Scotch" Brand acetate tape may be pressed against the surface bearing the positive particulate image and stripped away as shown in FIG. **5**. The pressure sensitive adhesive will carry with it those particles remaining on the surface softenable layer **2** and a small portion of softenable layer **2**. This sheet may then be laminated onto a white backing such as paper. Thus, a full color image conforming to the original is produced with areas exposed to white light such as area **9** appearing white due to the white backing and areas not exposed to light such as area **10** appearing black since particles of all colors remain. Alternatively, a masking material could be incorporated into softenable layer **2** to mask out the migrated particles.

Alternatively, softenable layer **2** may be softened by the application of heat by any suitable means. When layer **2** has softened sufficiently, particles migrate selectively as described above. The image may be fixed by merely cooling layer **2**, or the particles remaining on the surface may be stripped off with a pressure sensitive material as described above.

As is further pointed out in the examples below, the photosensitive particulate layer could be exposed to a color negative which would produce a reversal of the negative, i.e., a positive color image on the substrate. In such a case, a positive final image would be produced by merely washing away softenable layer **2** and unmigrated particles on the surface thereof with a solvent for said softenable layer **2**. Further, by varying process steps and materials, either positive-to-positive or positive-to-negative images may be produced.

The following examples describe specific embodiments of methods of producing color images using the process of this invention. Parts and percentages are by weight unless otherwise indicated. The following examples should be considered to describe preferred embodiments of the process of this invention.

EXAMPLE I

A mixture of two pigments is prepared by mixing finely-divided Indigo (a natural pigment available from National Aniline, division of Allied Chemical Company) and finely-divided Monostral Red B (a quinacridone pigment available from E. I. duPont de Nemours & Company) and ball milling until the average particle size is about 0.5 micron. These particles are then mixed with glass beads having an average diameter of about 50 microns. A plate is prepared by dissolving about 10 parts Staybelite Ester No. 10 a glyceryl tri-ester of 50 percent hydrogenated wood resin, from Hercules Powder Company, in about 50 parts toluene. This solution is flow coated onto the conductive surface of an aluminized Mylar (polyethylene terephthalate available from E.I. DuPont de Nemours & Company) film to a dry thickness of about 2 microns. The mixture of pigment particles and glass beads is then cascaded across the resin surface. A uniform pigment particle layer across the surface is produced. This layer is more firmly adhered to the resin surface by heating the plate to about 65°C. for about 3 minutes. The plate is cooled to room temperature, and then charged to a negative potential of about 190 volts by corona discharge as described by Carlson in U.S. Pat. No. 2,588,699. Then, alternate parallel strips of red, green and blue Wratten filter material are placed on the plate surface. The plate is then exposed through the filter strips by means of a tungsten lamp. Total exposure is about 260 foot-candle-seconds on the colored filters. The filter strips are then removed and the plate is developed by dipping it in a container containing Sohio Odorless Solvent 3440, a kerosene fraction available from Standard Oil of Ohio. After a few seconds in the solvent, the plate is removed. The resulting images have Indigo remaining in the areas under the red filter while Monostral Red particles remained under the green filter. Neither pigment remained in the areas under the blue filter. Thus, selective color response is observed with the particles which absorb the particular incident light remaining on the plate and those particles which do not absorb the particular incident light being washed away during development.

EXAMPLE II

A plate comprising a two micron layer of Staybelite Ester 10 on aluminized Mylar is prepared as in Example I. A particle mix is prepared by mixing equal portions of three finely-divided pigments; a cyan pigment, Diane Blue, C.I. No. 21180, 3,3'-methoxy-4,4'-diphenyl-bis (1''-azo-2''-hydroxy-3''-naphthanilide), available from Harmon Colors; a magneta pigment, Watchung Red B, 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3 -naphthoic acid available from E.I. duPont de Nemours & Company, and a yellow pigment, Lemon Cadmium Yellow, a cadmium sulfide pigment. After mixing, this "tri-mix" is ball milled for approximately 48 hours to ensure good mixing and uniform small particle size. About 10 parts of this mixture is then suspended in water and the suspension is sprayed onto the resin surface of the plate. A uniform, thin, black-appearing layer is thus formed on the resin surface. A metal roller at about 70°C. is rolled across the surface to soften the resin and ensure good adherence between the pigment particles and the resin. The plate is then charged to a negative potential of about 200 volts. A conventional "Kodachrome" transparency is placed in substantial contact with the plate. The plate is then exposed using a tungsten light producing about 250 foot-candle-seconds exposure on the transparency surface. The transparency is then removed and the plate is developed by exposing it to vapors of Freon **113**, trifluoro trichlorethane, available from E.I. duPont de Nemours & Company. After a few seconds, the plate is removed. It is observed that portions of the particles have migrated from the surface of the resin to the resin-aluminum interface. A piece of "Scotch" brand pressure sensitive tape is pressed against the surface of the resin and stripped away. Due to the solvent exposure, the Staybelite Ester 10 layer is relatively soft and breaks at about half its depth. Only those particles remaining at the surface of the resin layer are stripped away with the pressure sensitive tape. The image formed by these stripped-away particles is a positive colored image conforming to the original having good color balance and separation. A color negative is observed to remain on the plate. Thus, in this instance the migrated particles are those which absorb the incident light leaving behind, by subtractive color formation, a positive image at the plate surface.

EXAMPLE III

A sheet of aluminized Mylar is roll coated with a mixture of about 10 parts Piccotex 100, a vinyl toluene-alpha methyl styrene copolymer available from the Pennsylvania Industrial Chemical Company, in about 20 parts cyclohexane to a dry thickness of about 3 microns. A pigment tri-mix is prepared by mixing finely divided pigment particles of three colors; a cyan pigment, Diane Blue; a magneta pigment, Permagen Red L Toner 51-500, 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, available from E.I. duPont de Nemours and Company; and a yellow pigment, N-2''-pyridyl-813-dioxodinaphtho-(1-2-2',3')-furan-6-carboxamide, prepared as described in copending application Ser. No. 421,281 filed Dec. 28, 1964, now U.S. Pat. No. 3,447,922. This tri-mix is ball milled for about 48 hours to reduce the average particle size to about 0.3 micron. The pigment tri-mix is then mixed with glass balls having an average diameter of about 200 microns and the mixture is cascaded across the Piccotex 100 surface. A uniform thin layer of pigment particles is thus deposited on the resin surface. The plate is then heated to about 90°C. for about 2 minutes to firmly adhere the particles to the resin surface The plate is then charged to a negative potential of about 200 volts by corona discharge. The charged plate is exposed to a color negative by projection; the total exposure at the plate surface being about 200 foot-candle-seconds. The exposed plate is developed by immersion in cyclohexane for about 2 seconds. Upon removal from the solvent, a positive image conforming to the negative original is observed on the plate surface.

EXAMPLE IV

A mixture of finely-divided Indigo and finely-divided Monostral Red B is prepared by ball milling according to the procedure of Example I and dispersing the mixture in a solution of about ten parts of Staybelite Ester 10 in about **50** parts of toluene. A migration imaging member is prepared by coating this solution onto the surface of an aluminized Mylar substrate by means of draw coating to a dry thickness of about 4 microns. The thus prepared imaging member is employed in the imaging method of Example I except the member is charged to a negative potential of about 250 volts by a corona discharge device. The resulting images have Indigo remaining in the areas under the red filter while Monostral Red particles remain under the green filter. Neither pigment remains in the areas under the blue filter. Thus, selective color response is observed with the migration particles dispersed throughout the softenable layer in the same manner as when the migration particles are in a layered configuration. Those particles which do not absorb the particular incident light to which they are sensitive are washed away during the development procedure leaving the particles which absorb the particular incident light to which they are responsive on the Mylar substrate.

Although specific materials and conditions were set forth in the above exemplary processes of forming color images by photoelectrosolography, these were merely meant as illustrations of the present invention. Various other materials and process steps, such as those listed above, and various conditions may be substituted for those in the examples with similar results. For example, the photosensitive materials and the resin layers may be electrically or dye sensitized as desired.

Many 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 encompassed within the spirit of this invention.

What is claimed is:

1. A method of color imaging comprising the steps of:

a. providing an electrically insulating softenable layer having contact therewith a non-imagewise mixture of electrically photosensitive particles of at least two colors, said softenable material capable of having its resistance to migration of said photosensitive particles decreased sufficiently to allow migration of said photosensitive particles in depth in said softenable layer;

b. substantially uniformly electrostatically charging said softenable layer;

c. exposing said particles to an image pattern of polychromatic light; and

d. developing said member by decreasing the resistance to migration of said photosensitive particles through said softenable layer at least sufficient to allow migration of the photosensitive particles in depth in said softenable layer.

2. The method of claim **1** further providing a substrate toward which said particles migrate.

3. The method of claim 1 wherein said insulating layer is softened by the application of vapors which are a solvent for said insulating layer.

4. The method of claim 2 wherein after said portions of said particles have migrated, a receiving sheet having an adhesive surface is pressed against said particulate layer and is stripped away, carrying with it the unmigrated portions of said particles.

5. The method of claim 2 wherein said insulating layer is softened by contacting said insulating layer with a liquid which is a solvent for said insulating layer but not for said substrate and said particles, whereby the unmigrated particles and a substantial portion of said insulating layer are washed away.

6. The method of claim 1 wherein said insulating layer is softened by the application of heat.

7. The method of claim 1 wherein said particulate layer comprises a mixture of cyan colored particles sensitive mainly to red light, magenta colored particles sensitive mainly to green light and yellow colored particles sensitive mainly to blue light.

8. The method of claim 1 wherein the electrically photosensitive particles are embedded within the free surface of said insulating layer in a thin non-continuous layer.

9. The method of claim 1 wherein the electrically photosensitive particles are dispersed throughout the insulating softenable layer.

10. The method of claim 1 wherein the insulating softenable layer has a thickness of from about 1 to about 4 microns.

11. The method of claim 2 wherein said substrate is provided during electrostatic charging of said softenable layer.

12. The method of claim 2 wherein said portion of said particles migrate to the surface of said substrate.

13. The method of claim 1 wherein the electrically photosensitive particles comprise a photoconductive outer coating over an inert inner core.

14. The method of claim 1 wherein said electrically photosensitive particles have an average particle size of from 0.01 to about 2 microns.

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